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(U) Synthesis of Inorganic Oxidizers

Final Summary Report

by

E. M. Gardner, E. Pazioszek, et al.
Pennsalt Chemicals Corporation

June 1966

Air Force Systems Command
Research and Technology Division
Rocket Propulsion Laboratory
Edwards, California

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(U) Synthesis of Inorganic Oxidizers

Final Summary Report

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D. M. Gardner, E. Bartoszek, et al.
Pennsalt Chemicals Corporation

June 1966

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This report was prepared by Pennsalt Chemicals Corporation's Research and Development Department, King of Prussia, Pennsylvania, under USAF Contract No. AF 04(611)-8518. The program was initiated under Project No. 3148, Task No. 314804 and bears ARPA Order No. 352 (Amend. #4). The project engineer is Dr. William Leahy, RPCS.

This Final Summary Report covers the period August 1, 1962 to April 1, 1966.

The principal scientists who worked on the project over the whole period were E. Bartoszek, C. Mackley, E. Hillman, and O. Sprout. Analytical work was supervised by W. Clavan and J. Smith. This report was prepared by these men and D. M. Gardner, project supervisor, and was approved by W. M. Lee, Director of Contract Research.

This report references the following documents which are all classified Confidential, Group 4 (our reference numbers): 3a, 11, 16, 23, 25 and 28.

This technical report has been reviewed and is approved.

GEORGE F. BABITS, Lt. Colonel, USAF
Chief, Propellant Division

Abstract

The objective of the work was to prepare new oxidizers composed of combined forms of chlorine, oxygen, and fluorine. Emphasis was placed on the use of ClF_3, ClF_5, ClO_2F, and ClO_3F as starting materials. Experimental techniques included high pressure-high temperature reactions, arc and glow discharge reactions and electrochemical reactions in inter-halogens and other active fluorinating solvents.

Attempts to form salts of the alleged ClO_3F^{-2} and $ClO_2F_2^{-1}$ ions by the reported interaction of chlorates and fluorides were not successful. No evidence for the existence of the salts was found after rigorous elemental, infrared and X-ray analysis of the products. It is concluded that these salts cannot be prepared by the methods reported in the literature.

The heat of combustion of NH_4ClO_4 with CO has been measured and from the data the standard heat of formation of NH_4ClO_4 is calculated to be -71.13 kcal./mole with an estimated uncertainty of 0.32 kcal. This confirms the earlier reported values of -70.74 ± 0.32 (A. A. Gilliland and W. H. Johnson, J. Research Nat'l Bur. Standards, 65A, 67 (1961) and -70.63 kcal. (M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960)) obtained from solution-calorimetric measurements.

ClO_3F did not react with the following compounds under a variety of high pressure and temperature conditions although in many cases thermal degradation occurred: SbF_5, SF_6, BF_3, ClF_3, F_2, $CsClF_4$, ClF_5, ClF_4SbF_6 and NO_2F. Additional attempts to fluorinate ClO_3F with F_2 in an electric discharge were unsuccessful.

The laboratory procedure for the safe preparation of ClO_2F, which was used as an intermediate, was developed to yield 3.0 grams per day. Liquid ClO_2F will react with metal storage vessels and decompose to ClO_3F, ClO_2 and Cl_2. Storage is best carried out at $-80°C$.

ClO_2F was partially fluorinated by elemental fluorine and not fluorinated by chlorine pentafluoride, chlorine trifluoride, cesium tetra-fluorochlorate and cesium fluoride under a variety of temperature and pressure conditions. From the results of experiments with ClF_5-ClO_2F, it appears that ClO_2F will induce the thermal decomposition at temperatures as low as $230°$. Under similar conditions ClF_5 is stable to $350°$.

NO_2F reacts with ClO_2F over a period of 4 days at $-78°$ to form a solid adduct with a melting point of $-22°$ and a vapor pressure of 740 mm. at $0°$. The solid and its melt is insoluble in ClF_3.

Attempts to prepare novel Cl-F compounds by pyrolysis of ClF_3 and subjecting ClF_3 and mixtures of ClF_3 and F_2 to electrical discharges and gamma irradiation were unsuccessful. ClF_3 was not affected by O_2 in a spark or corona discharge and contact with ozone at $-78°$.

In a supporting study nitryl tetrafluorochlorate, NO_2ClF_4, was prepared by reaction of NO_2F with ClF_3 at $-78°$. The vapor pressure was measured from $-50°$ (30 mm) to $+25°$ (1360 mm) and can be expressed by the equation:

$$\log_{10} p \text{ (mm)} = 7.945 - \frac{1436}{T}$$

From these data the equilibrium constant is calculated to be 0.250 atmospheres at $+9.5°C$.

$$\log_{10} Kp = 9.409 - \frac{2840}{T}$$

The apparent heat of dissociation to NO_2F and ClF_3 is $+13$ kcal/mole.

As in the case of ClF_3, attempts to prepare novel Cl-F compounds using ClF_5 as an intermediate were unsuccessful. These involved fluorination, pyrolytic, and discharge techniques and the following reactants: F_2, CsF, ClF_3. In addition ClF_5 did not react with the following oxygen-containing compounds although in many cases degradation of the ClF_5 occurred: O_2, O_3, ClO_2F, ClO_3F, $KClO_3$, $KClO_4$, and $CsClO_4$.

NO_2F reacted with ClF_5 at low temperatures to give a 1:1 liquid adduct possessing a vapor pressure of one atmosphere at $-28°$. The liquid product is not a simple solution since the vapor pressure at all temperatures is considerably lower than that predicted by Raoult's law, e.g. observed, 5 mm at $-78°$: predicted, 292 mm.

ClF_5 reacts with SbF_5 to produce ClF_4SbF_6, m.p. $34-35°$, which is analogous to ClF_2SbF_6, m.p. $225-228°$. Both materials are reactive with all but highly fluorinated materials. On storage in Kel-F containers ClF_4SbF_6 (and to a lesser extent ClF_2SbF_6) will induce extreme stress cracking of the plastic within hours.

ClF_5 did not form a complex with SF_4, SF_6, or BF_3 stable at ambient temperature.

Nitrogen trifluoride, NF_3, did not react with the following compounds at temperatures in the general range $200°-475°C$ and pressures of 650-2125 psig: ClF_3, ClF_5, ClO_3F, $CsClF_4$, ClF_2SbF_6, and ClF_4SbF_6.

Tetrafluorohydrazine is a reductant for the series of chlorine fluorides at 25C° according to the equations

$$N_2F_4 + ClF_5 \longrightarrow 2NF_3 + ClF_3$$

$$N_2F_4 + ClF_3 \longrightarrow 2NF_3 + ClF$$

$$N_2F_4 + 2ClF \longrightarrow 2NF_3 + Cl_2$$
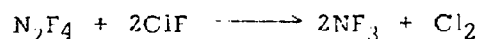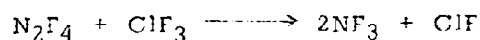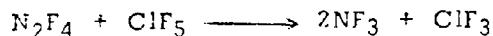
Reactions of complexes of ClF_5 and ClF_3 (ClF_4SbF_6, $CsClF_4$, ClF_2SbF_6) with N_2F_4 involve first a thermal decomposition of the complex followed by fluorination of N_2F_4 by the free chlorine fluoride.

N_2F_4 and ClO_2 react at 25° in a flow system to produce NOF and Cl_2.

The trans isomer of difluorodiazine did not react with ClO_3F, or ClF_5 at temperatures from -78° to 250°C. With ClO_2F, trans-N_2F_2 did not react in the range -78° to 25° but at 200°, reaction occurred resulting in the formation of ClF_3, NF_3, N_2, and O_2.

Cis-difluorodiazine did not react with the following compounds in the range -78° to +150°C: ClO_2F, ClO_3F, OF_2, ClF_5, ClF_3, and ClF. At or above 150°, thermal decomposition of N_2F_2 to N_2 and F_2 became appreciable resulting in the fluorination of the coreactants ClF_3 and ClF.

Oxygen difluoride, OF_2, did not react with the following compounds at temperatures in the general range 150°-250°C and pressures of 500-2950 psig: ClF_3, ClF_5, ClO_2F, ClO_3F, NF_3, SbF_5, CsF, $CsClF_4$, ClF_2SbF_6, ClF_4SbF_6. In most experiments some thermal decomposition of the OF_2 to O_2 and F_2 took place and the extent of the decomposition increased with temperature. Oxygen difluoride reacted with the simple chlorides NaCl, CsCl, and $CaCl_2$ to form the corresponding fluorides and to liberate O_2 and Cl_2.

$$OF_2 + 2MCl \longrightarrow 2MF + 1/2\,O_2$$
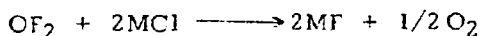
The reaction was very exothermic between $CaCl_2$ and OF_2 below room temperature.

Oxygen difluoride did not react with Cl_2 or ClF at 25°C; however, at 150°, in a static system, these formed ClF and ClF_3, respectively, in addition to oxygen and a small amount of ClO_2F.

The fluorination of ClO_2 in a flow system with ClF_5, NF_3, and OF_2 was studied with the following results: ClF_5 produced ClO_2F, Cl_2, and O_2; NF_3 did not react; and OF_2 formed ClF_5, ClO_2F, and ClO_3F.

In contrast the fluorination of Cl_2O with either F_2 or OF_2 in a static system at, respectively, $155°$ and $130°$ produced the new oxidizer, trifluorochlorine oxide, $OClF_3$.

A study was carried out to determine the feasibility of preparing new oxidizers by electrolysis of systems containing as solvents or solutes ClF_3, ClF_5, ClO_2F, ClO_3F and other halogen fluorides. The feasibility of this approach was partially demonstrated by the preparation of ClF_5 by electrolysis of ClF_3 containing either CsF or SbF_5 as solutes at $0°C$.

Unfortunately many of the halogen fluorides and halogenyl fluorides of interest as solvents and reactants are poor conductors, and the electrical equivalents which can be passed through a system are extremely small per unit time. The conductivities of ClF_3, BrF_3, ClF_5, SbF_5, IF_5, ClO_3F, BrF_5, NO_2F, and HF are, respectively (ohm^{-1} cm^{-1}): 4×10^{-7} ($0°$), 7.53×10^{-4} ($25°$), $<2.11 \times 10^{-7}$ ($-23.9°$), $<2.11 \times 10^{-7}$ ($25°$), 5.65×10^{-5} ($25°$), $<2.1 \times 10^{-9}$ ($-51°$), 2.73×10^{-6} ($25°$), $<10^{-6}$ ($-78°$), $<10^{-6}$ ($-12°$).

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Synthesis of Inorganic Oxidizers

I. INTRODUCTION

This research was directed to the preparation of solid oxidizers composed of combined forms of chlorine, oxygen, and fluorine. In particular, we were interested in those ions or compounds in which chlorine as a central atom is coordinated with four, five, or six ligand atoms. The elements most suited and most desired for combination with chlorine are fluorine, oxygen, and nitrogen because of their relatively low atomic weight, high oxidizing potential and their suitable dimensions and electronegativities as illustrated below:

	$\underline{O}$	$\underline{F}$	$\underline{N}$
Atomic weight	16	19	14
Relative electronegativity	3.5	4.0	3.0
Atomic covalent radius (A)	0.74	0.72	0.74
Cl-X bond strength (kcal)	49	41	48

The similarity of the above properties implies that there may be little entropic or enthalpic objections to the substitution of one element for either of the other elements under the proper circumstances. Known species like perchloryl fluoride, ClO_3F, and the perchlorylamide ion, ClO_3N^{-2}, indicate the plausibility of seeking new oxidizers by the principal of substitution of nitrogen or fluorine for oxygen in the several oxides and ions of chlorine. Other examples are chloryl fluoride, ClO_2F, and the chlorylamide ion, ClO_3NH^-, and schematic relations are outlined below:

| perchlorate | perchloryl fluoride | perchlorylamide |

| chlorate | chloryl fluoride | chlorylamide |

- 1 -
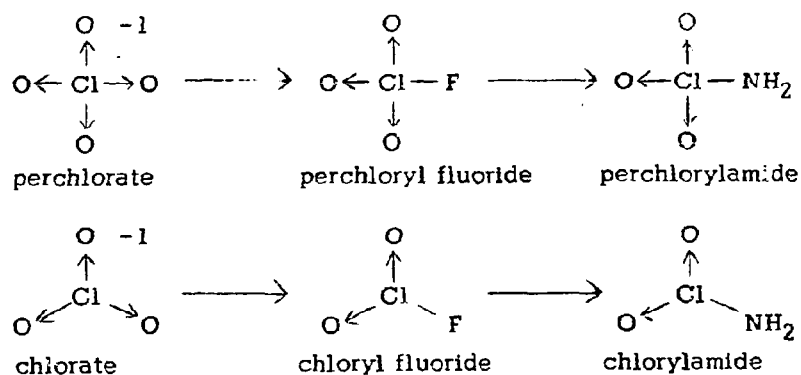
The similarity of the oxide and fluoride ions in such structures is il. ·strated by the formation of ClO_3F and the fact that it is a stable, symmetrical molecule of nearly zero dipole moment (Ref. 1). In addition, the similarity of O and F is so close that the molecule has difficulty in distinguishing between the two and a somewhat random orientation exists in the crystal at low temperatures, resulting in a small, but measurable, zero point entropy (Ref. 2). Less is known about the equivalence of nitride and fluoride ions although ClO_3N^{-2} forms many stable, but shock sensitive, salts.

By analogy, it is possible to propose a number of feasible oxidizers by application of this "substitution principle" to known compounds and ions containing chlorine in its normal valence states. Of particular interest are ClO_3F^{-2}, $ClO_2F_2^-$, $OClF_3$, $OClF_2^+$, ClF_4^+, $OClF$, etc., which were considered as target oxidizers for this synthesis program.

In addition, the synthesis of chlorine pentafluoride, ClF_5, (Ref. 3) has indicated that a variety of novel oxidizers might be prepared using this material as an intermediate. Like BrF_5 (Ref. 4), ClF_5 is reported to have the same pyramidal configuration (Ref. 3b). Pauling suggested that in a structure of this type the bonds are directed toward the five corners of a square pyramid which, with the unshared pair, would form an octahedron (Ref. 5, page 180).
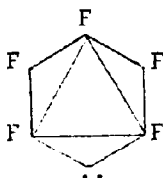
Presumably this material could function as a base toward Lewis acids more electrophilic than ClF_5 itself. We have been interested in forming adducts of ClF_5 with O, NO_2, NO, SbF_5, etc In addition, we examined the possibility of the formation of stable salts containing the ClF_4^+ and ClF_6^- ions.

Our studies have involved the use of ClF, ClF_3, ClF_5, ClO_2F, ClO_2, Cl_2O, and ClO_3F as starting materials and the experimental techniques being used include high pressure (ca 6000 psig), high temperature (up to 500°C), corona and arc discharges, flow reactions at ambient pressure, and electrochemical reactions in interhalogen solvents.

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II. RESULTS AND DISCUSSION

A. Attempted Synthesis of Trioxofluorochlorate(V) and Dioxodifluoro-
chlorate(V) Salts

The initial phases of this program were directed toward the
preparation of trioxofluorochlorate(V), ClO_3F^{-2}, salts containing
combustible cations. Of particular interest were $(NH_4)_2ClO_3F$,
$(N_2H_5)_2ClO_3F$, $[(CH_3)_4N]_2ClO_3F$, etc. It was planned to synthesize
these salts in amounts sufficient for complete physical and thermo-
chemical evaluation including the determination of heats of combustion
or reaction with appropriate gases (O_2, CO). This would permit a
thorough evaluation of the theoretical performance of these salts as
oxidizers in solid propellants.

The only salts reported to date presumed to contain the ClO_3F^{-2}
ion are the supposed soluble and hygroscopic hydrates of $CuClO_3F$,
$ZnClO_3F$, $NiClO_3F$, and $CoClO_3F$ and the insoluble and nonhydrated
$CaClO_3F$ and $BaClO_3F$ (Ref. 6-11). Chemical, analytical and
crystallographic data relating to and supposedly indicating these
compositions and structures are given.

The metal trioxofluorochlorates were primarily of interest as
useful intermediates in the preparation of combustible salts and the
initial work was devoted to the preparation of pure samples of trioxo-
fluorochlorates suitable for conversion to the $(NH_4)_2ClO_3F$,
$(N_2H_5)_2ClO_3F$, etc. mentioned above.

It is reported that the preparation of the metal salts is carried
out by digestion of an aqueous solution of the metal chlorate with the
stoichiometric amount of the sparingly-soluble metal fluoride at 85°-
90°. Addition of nitric or acetic acid is required to effect solution
of the fluoride.

$$M(ClO_3)_2 + MF_2 \longrightarrow 2MClO_3F \quad (M=Cu, Zn, Ni, Co)$$

The digestion is reportedly carried out in either Teflon or
platinum ware and the resulting clear solution is cooled to room tem-
perature and slowly evaporated to near dryness in a paraffin-coated
desiccator using either sulfuric acid as a desiccant or vacuum drying.
Crystallization of the alleged trioxofluorochlorate is supposed to begin
after 75-80% of the water is evaporated.

As an alternative to the use of metal trioxofluorochlorates as
intermediates, studies were conducted to determine whether con-
centrated aqueous solutions of HF and $HClO_3$ could be reacted

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directly to produce the aqueous acid, H_2ClO_3F. Attempts were also made to prepare the free acid by passing aqueous solutions of salts believed to be trioxofluorochlorates through columns containing strong cation exchange resins (Amberlite IR-120, Rohm and Haas).

Since it is reported that the related dioxodifluorochlorate (V) salts, $ClO_2F_2^{-1}$, can be prepared in a similar manner by the simple technique of using an excess of hydrogen fluoride during the digestion step, analogous studies were directed toward the preparation of these salts as well.

$$ClO_3^- + 2HF \longrightarrow ClO_2F_2^- + H_2O$$
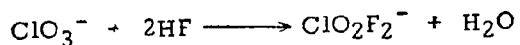
However, it is also reported that the dioxodifluorochlorate (V) salts are in equilibrium with trioxofluorochlorate (V) salts in solution and that each may be prepared from the other by a simple shift in conditions.

$$ClO_2F_2^- + H_2O \longleftarrow ClO_3F^{-2} + HF + H^+$$
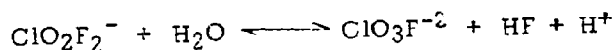
For this reason the bulk of our experimental work was devoted to the preparation and characterization of the trioxofluorochlorates and only a minor effort was spent on studying methods for the preparation of the dioxodifluorochlorates.

In the first few months of this program crystals were obtained by using the reported procedures and elemental analyses were obtained which evidently confirmed the existence and composition of the reported trioxofluorates. Typical analyses received are given below:

		% Cation	$\%ClO_3$	%F
"$CuClO_3F \cdot 5H_2O$:"	Found	23.9%	32.0	5.1
	Theory	24.8	32.6	7.4
"$NiClO_3F \cdot 6H_2O$:"	Found	22.0	31.0	7.0
	Theory	21.8	32.5	6.6
"$ZnClO_3F \cdot 4H_2O$:"	Found	29.2	27.2	5.2
	Theory	27.3	34.8	7.9

Superficially, the analyses found are in reasonably good agreement with the theoretical values. However, during our studies it became apparent by qualitative tests and X-ray diffraction patterns

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that these isolated materials were actually fortuitous mixtures of chlorates with corresponding metal fluorides and/or fluosilicates. It has been demonstrated at this laboratory that the use of paraffin-coated or halocarbon wax-coated desiccators for evaporation of HF-containing solutions (the procedure used by previous workers) will result in contamination of the solutions by SiF_6^{-2} ions. It is preferred to use plastic desiccators for work with HF solutions. In addition it is to be noted that New York University personnel report that ClO_3F^{-2} salts are isomorphous with fluosilicates and give X-ray patterns that are identical with those of the corresponding fluosilicates. It is important to note that during our work it was found that up to 10% $Ba(ClO_3)_2$ in $BaSiF_6$ could not be detected by using infrared absorption spectra unless the analyst was warned beforehand and used special techniques. In X-ray analysis up to 20% $Ba(ClO_3)_2$ could not be detected as a result of simple dilution. Consequently mixtures of $BaSiF_6$ and $Ba(ClO_3)_2$ could appear to be a single salt with a diffraction pattern identical with the fluosilicate but which would give strong oxidizing tests and evolve chlorine oxides on treatment with sulfuric acids as would be expected for a trioxofluorochlorate (V) salt.

A re-examination of the materials analyzed in the above table and similar products invariably showed the presence of silicon in amounts (1-2%) required for the presence of the necessary quantity of fluosilicate salt.

Our work involved the attempted preparations of the intermediates, $CuClO_3F \cdot 5H_2O$, $NiClO_3F \cdot 7H_2O$, and $ZnClO_3F \cdot 7H_2O$ and particular trioxofluorochlorates of direct interest such as $(NH_4)_2ClO_3F$,
$$[(CH_3)_4N]_2ClO_3F, \text{ and } (NH_2\overset{\overset{\displaystyle NH}{\|}}{C}NH_3)_2ClO_3F.$$

However, all attempts to reproduce the preparation of ClO_3F^{-2} and $ClO_2F_2^{-1}$ salts were unsuccessful and it is our conclusion that these salts cannot be prepared by the methods reported. A theoretical consideration of the valence election configuration of the chlorine atom in the ClO_3F^{-2} and $ClO_2F_2^{-1}$ ions indicates that these ions can only be formed by utilization of the available 3d orbitals in chlorine by unpairing 3p electrons and promoting one of the pair to the higher energy 3d orbital prior to bonding with oxygen and fluorine atoms. It may be possible that these ions could be formed under unusual conditions but it appears unlikely that the ClO_3F^{-2} and $ClO_2F_2^{-1}$ ions can be prepared in aqueous systems below 100°C as reported.

Our failures to prepare the materials prompted us to obtain samples from Dr. A. Ray (Visiting Fellow, New York University, 1962-63) which were reputed to be $NiClO_3F \cdot 4H_2O$ and Gu_2ClO_3F (Gu represents the guanidinium cation, $NH_2C(NH)NH_2^+$). In all, three samples were obtained of 100-200 mg. each and these are discussed below:

"$NiClO_3F \cdot 4H_2O$" (First Sample)

A sample of allegedly pure $NiClO_3F \cdot 4H_2O$ was received from Dr. Ray and his co-workers and infrared X-ray analysis indicated the sample to be $NiSiF_6 \cdot 6H_2O$. Since the ClO_3F^{-2} salts are claimed to be isomorphous with fluosilicates a chemical analysis for silicon was performed. Found: 9.1% Si (theoretical for $NiSiF_6 \cdot 6H_2O$, 9.05% Si).

Qualitative analysis indicated no oxidizing power of the sample following dissolution in water.

"$NiClO_3F \cdot 4H_2O$" (Second Sample)

Approximately 0.2 g. of a second sample of $NiClO_3F \cdot 4H_2O$ was obtained from Dr. Ray and the results of analysis are as follows:

	Theory for "$NiClO_3F \cdot 4H_2O$"	Reported by N.Y.U.	Found
Cl	15.2	15.3	14.2
F	8.1	9.5	9.2

An aqueous solution of the material proved to be strongly oxidizing in a qualitative test with aniline sulfate solution (indicative of a chlorate or similar oxidizing ion in solution).

An X-ray analysis of the sample as received indicated the presence of $NiSiF_6 \cdot 6H_2O$ and an unknown material.

On the assumption that the sample was a mixture of hydrated $NiSiF_6$ and $Ni(ClO_3)_2$ (to explain the qualitative tests reported by Dr. Ray) a mixture was formulated with the following composition based on the chemical analysis:

$Ni(ClO_3)_2 \cdot 4H_2O$ — 64.8% (by weight)
$NiSiF_6 \cdot 6H_2O$ — 35.2%

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The nickel chlorate was a special preparation and was dehydrated below the normal hexahydrate. Formulation of the above mixture was based on the relative amounts of the Cl and F as found in the N.Y.U. sample.

An X-ray analysis of the fresh mixture showed the presence of the two components. However, on exposure to atmospheric moisture the mixture adsorbed water and an X-ray pattern of the exposed mixture was identical to that obtained for the sample from Dr. Ray and his co-workers.

The sample was thus a mixture of $NiSiF_6 \cdot 6H_2O$ and a hydrate of $Ni(ClO_3)_2$.

"Gu_2ClO_3F"

A sample (ca. $0 \cdot 2g$) designated "Gu_2ClO_3F" was provided to Pennsalt by Dr. Ray on July 17, 1963. Elemental analysis is given below:

	Theory for "$(CN_3H_6)_2ClO_3F$"	Reported by Ray	Found
Cl	15.9	15.3	14.2
F	8.5	9.45	9.2
Si	0.0	---	0.0

X-ray diffraction analysis of the Ray sample yields an unknown pattern that does not resemble the pattern of guanidinium fluosilicate that had been prepared as a reference. It is to be noted that Ray reports the ClO_3F^{-2} salts are isomorphous with fluosilicates and give X-ray patterns that are identical with those of the corresponding fluosilicates.

Infrared analysis indicates a basic guanidinium structure for the cation; however, guanidinium salts shown a broad infrared absorption band centering at about 6μ and a weaker, sharper band at $6.4-6.5\mu$. This latter band is absent in the infrared spectrum of the sample; curiously, it appears to be absent from the reported guanidinium thiocyanate spectrum also (Ref. 12). It is believed that some modification to the guanidinium cation has occurred during the supposed preparation of the trioxofluorochlorates and especially during the digestion in the hot acid oxidizing solution. It is suggested that the cation is a polybasic condensed guanidine or a higher homolog of biguanide. Unfortunately, the small sample size prevented a thorough characterization of the material.

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't is interesting to note that from the 15 attempted preparations of Gu_2ClO_3F at this laboratory and over 60 crystal fractions obtained, only three isolated crystal crops (totaling about 200 mg.) have been separated and identified as the same material as the N.Y.U. sample.

In conclusion, no evidence has been obtained for the preparation to date of either trioxofluorochlorate or dioxofluorochlorate salts based on extensive studies at this laboratory and examination of products claimed to be these materials. Therefore, all work involving preparation of these salts in aqueous solution was terminated.

It should be noted, however, that the structures of the ClO_3F^{-2} and $ClO_2F_2^{-1}$ ions are reasonable and it may be assumed that salts of these ions will probably be prepared using different procedures than those reported. This work was continued in studies on the fluorinations of chlorine oxides and oxygenations of chlorine fluorides and the unsuccessful results are summarized in later sections of this report.

B. Thermochemical Measurements

Heat of Formation of Ammonium Perchlorate

A primary objective of the program was to evaluate new oxidizers as propellants and, apart from determining the stability and chemical reactivity of the new oxidizers, this is most positively accomplished by measurement of heats of combustion and/or reaction followed by calculations of heats of formation from these data.

The pilot work was carried out using NH_4ClO_4 since this was representative of the type of oxidizer to be prepared. In addition, although accurate heats of formation of NH_4ClO_4 have been determined from solution-calorimetric measurements (Ref. 13, 14) no data for the heat of combustion of NH_4ClO_4 have been reported.

Carbon monoxide was chosen as a fuel gas partially on the basis of its availability, ease of handling, and high purity and partially because a preliminary evaluation of the heat of combustion with NH_4ClO_4 indicated that the heat evolved would be comparable with that expected for hydrogen according to the following equations:

1. $NH_4ClO_4 (s) + 2.5 H_2 (g) \longrightarrow 0.5 N_2 (g) + HCl (aq.) + 4 H_2O (l)$

$$\triangle H = 2.5 \text{ kcal./g. } NH_4ClO_4$$

- 8 -

2. NH_4ClO_4 (s) + 2.5CO — ~0.5N_2 (g) + HCl (aq.) + 1.5H_2O (l) + 2.5CO_2
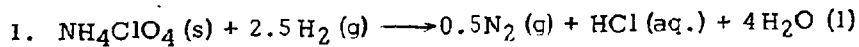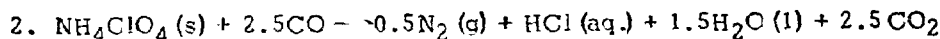
$$\triangle H = 2.04 \text{ kcal./g. } NH_4ClO_4$$

It appears that CO is a useful fuel gas and may be applicable to a variety of oxidizers (Ref. 15, 16). However, it must be noted that the combustion of oxidizers, such as NH_4ClO_4, containing hydrogen yields high temperature water vapor which can undergo a water-gas reaction with the excess CO present with the bomb.

3. $CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$ $\triangle H^{298} = -9.84 \text{ kcal.}$
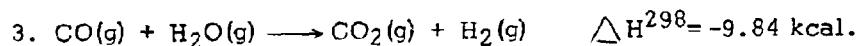
In the final analysis of the combustion data for the equation 2. above, corrections must be applied for the amount of water vapor entering into the water-gas reaction, noted in eq. 3. This correction is calculated according to the following equations:

H_2O (liq.) $\longrightarrow H_2O$ (g) $\triangle H^{298} = +10.520;$ $\triangle E^{298} = +9.930 \text{ kcal.}$

$CO(g) + H_2O$ (g) $\longrightarrow CO_2$ (g) + H_2 (g) $\triangle H^{298} = -9.840;$
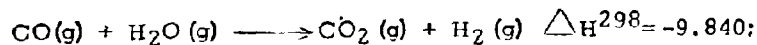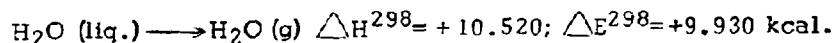
$$\triangle E^{298} = -9.840 \text{ kcal.}$$

$$\Sigma \triangle E = +.088 \text{ kcal./mole } CO_2.$$

The data obtained are presented in Table 1. The $\triangle E$ of the combustion process is 2033 cal./g. NH_4ClO_4 or 238.87 kcal./mole NH_4ClO_4. This corresponds to an enthalpy of combustion, $\triangle H_c^{298}$, equal to -238.57 kcal. with an estimated uncertainty of $\pm$ 0.32 kcal.

Using the values -38.139*, -26.4157, -94.0518, -68.3174 and 57.7979 kcal. for the standard heats of formation of, respectively, aqueous HCl, CO(g), CO_2(g), H_2O (liq.), and H_2O (g), the standard heat of formation of NH_4ClO_4(c) at 25°C is calculated to be -71.13 $\pm$ 0.32 kcal./mole.

The value -71.13 $\pm$ 0.32 kcal. is in good agreement with the reported solution-calorimetric values -70.74 $\pm$ 0.32 (Ref. 13) and -70.63 kcal. (Ref. 14) for the standard heats of formation of NH_4ClO_4.

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* (The heat of formation of HCl (aq.) was graphically determined from the data presented in N.B.S. Circular 500 and for the average concentration taken to be one mole HCl per 7.19 moles water as determined by analysis).

TABLE I

Combustion of NH_4ClO_4 with CO

Wt. NH_4ClO_4 g.	ΔT °C.	Wt. CO_2 Found, g.	Wt. CO_2 water-gas reaction, g.	Ignition Energy cal.	ΔE^a Gross cal.	ΔE water-gas reaction, cal.	ΔE^b corrected cal.	$\frac{\Delta E \text{ corr.}}{\text{g. } NH_4ClO_4}$
1.0769	0.892	1.2222	0.2144	1.6	2189	+.43	2189	2033
0.9222	0.765	1.0824	0.2198	1.6	1877	+.44	1877	2035
1.0714	0.888	1.3339	0.3313	1.6	2179	+.66	2178	2033
1.0658	0.880	1.2329	0.2348	1.6	2159	+.47	2159	2026
1.0287	0.854	1.2091	0.2462	1.6	2095	+.49	2095	2037

Average: 2033 cal./g.

Standard deviation of the mean: 1.91 cal./g.

NOTES:

a. Calorimeter constant = 2455.5±2.8 cal./°C.

b. $\triangle$ E Gross $-$ $\triangle$ E water gas

It is to be noted that the heat capacity of the calorimeter, 2455 ± 2.8 cal./°C, was determined by the combustion of benzoic acid in oxygen under certificate conditions. The correction in the heat capacity of the calorimeter due to a substitution of CO for O_2 amounts to 0.025 cal./°C and was considered negligible.

C. Investigations of the Preparation of Derivatives of Perchloryl Fluoride

Perchloryl fluoride might appear to be a promising intermediate in the preparation of new oxidizers, but its symmetry and the near equivalence of the Cl-O and Cl-F bond energies are serious handicaps. To date, it is impossible to selectively activate and cleave either a Cl-O or a Cl-F bond by such physical means as heat, pressure, electric discharges, ultraviolet radiation, gamma radiation, etc. If the minimum energy is achieved, uncontrolled decomposition occurs resulting in products representing almost every stable combination of the component elements including ClO_2F, ClO_2, ClF_3, ClF, Cl_2, O_2, and F_2. Chemically, it is known that unstable complexes can be formed with various bases such as phosphines, sulfides, and amines; however, these rapidly degrade with subsequent oxidation of the organic compounds to phosphine oxides, sulfoxides (and sulfones), and Schiff's bases or enamines. In several isolated instances, intermediates in the degradation processes have been found stable and have been fully characterized (Ref. 17).
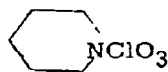
N-perchloryl piperidine
(sensitive compound,
explodes on warming
to 80° C)
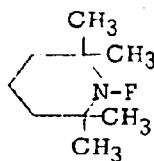
N-fluoro-2,2,6,6-tetramethyl-
piperidine-4-one
b.p. 60-61°/1.3 mm
Stable liquid

In contrast, attempts to fluorinate perchloryl fluoride with a variety of fluorinating agents under a variety of conditions have been unsuccessful. These experiments are discussed below.

Perchloryl fluoride was reacted with SbF_5 in a monel autoclave at 260° in an attempt to activate and fluorinate the ClO_3F molecule by the strong Lewis acid. On cooling it was found that no reaction had occurred. The charge was again heated at 420°C for 15 hours,

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and after cooling, the volatile products were identified as O_2 and Cl_2. A voluminous yellow-green solid filled the reactor and was subsequently characterized as a mixture of SbF_5 and complexes of SbF_5 with various metal fluorides. The solid phase contained barely 1.4% chlorine. Apparently a complete decomposition of the ClO_3F occurred triggered by the presence of SbF_5.

$$2ClO_3F \xrightarrow[420°]{SbF_5} Cl_2 + 3O_2 + F_2$$

$$1/2\, F_2 + M \text{ (reactor metal)} \longrightarrow MF$$

$$MF + SbF_5 \longrightarrow M\,SbF_6$$
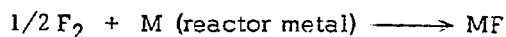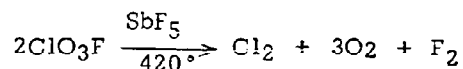
With the same objective, equimolar mixtures of ClO_3F and SbF_5 were treated with an equivalent amount of ClF_3 at temperatures up to 420°, generating autogenous pressures from 700 to 4000 psig. On cooling to 25°, the ClO_3F was recovered unchanged and the ClF_3 was found to have reacted with the SbF_5 to form ClF_2SbF_6. It is interesting to note that complex formation by SbF_5 completely destroyed its catalytic effect on the decomposition of ClO_3F. There is no doubt therefore that the strong Lewis acid caused an activation or polarization of the ClO_3F molecule in the previous experiment.

Similar reactions with weaker Lewis acids than SbF_5 were carried out in attempts to isolate either a complex of ClO_3F or to effect a more controlled fluorination without decomposition. ClO_3F did not react with either SF_6 or BF_3 at temperatures up to 330°. ClO_3F, however, did oxidize SF_4 at 375° to produce a very small amount of SF_6. When ClO_3F, ClF_3, and SF_4 were reacted together at 310°, oxidation of the SF_4 occurred and a variety of products were obtained including SF_6, SOF_4, SO_2F_2, Cl_2, O_2, and SOF_2.

In efforts to force a fluorination of ClO_3F with the reactive ClF_2^+ ion, equimolar ternary mixtures of $ClO_3F/ClF_3/SF_6$ and $ClO_3F/ClF_3/BF_3$ were each heated to 310° in a monel autoclave. On cooling the reactants were essentially recovered unchanged except that in the latter system the ClF_3 had reacted with BF_3 to form the stable ClF_2BF_4. The reaction reported in the paragraphs above involving a mixture of ClO_3F, ClF_3, and SbF_5 is also representative of this line of attack.

ClO_3F was reacted with a mixture of ClF_5 and SbF_5 in an experiment to observe the effects of the ClF_4^+ ion.

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$$ClF_5 + SbF_5 \longrightarrow ClF_4^+SbF_6^-$$

Maximum conditions were 375° and a pressure of 2000 psig. The major products found were ClF_2SbF_6, ClO_3F, and F_2 indicating the following reactions:

$$ClF_4^+SbF_6 \longrightarrow ClF_5 + SbF_5$$

$$ClF_5 \longrightarrow F_2 + ClF_3$$

$$ClF_3 + SbF_5 \longrightarrow ClF_2SbF_6$$
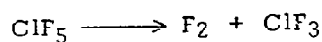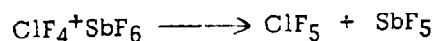
Since ClF_2^+ did not cause a fluorination of ClO_3F, it did not appear likely that the complementary base ClF_4^- would have any effect on ClO_3F. However, this was investigated using $CsClF_4$ prepared from a pressure reaction of ClF_3 with CsF. Solid $CsClF_4$ did not react with gaseous ClO_3F at temperatures up to 300° and pressures up to 450 psig. The ClO_3F was recovered quantitatively; however, some slight decomposition of the $CsClF_4$ occurred resulting in attack of the stainless steel reaction vessel and formation of red Cs_2NiF_6 (Ref. 18, 19).

A further attempt to fluorinate the ClO_3F molecule was made using an electric discharge. The apparatus employed is shown in Fig. 1. The unit is a stainless steel cylinder with 1/2" i.d. and a total volume of about 30-35 ml. The platinum electrode (18 gauge) passes through a Kel-F gland and insulator and forms a gap of 1/4". A side arm to the cylinder permits charging and removal of gaseous products. The gland and nut design allows complete removal of solid products and inspection of the cell interior. All experiments were of 24 hours duration and utilized an external resistance of 37.4 megohms (unless otherwise noted) to stabilize the discharge and to permit long term operation without overloading the circuit (30 kv. and 2000 microamps). The ClO_3F and F_2 were measured out on the basis of pressure such that the total pressure was about one atmosphere and the ratio of ClO_3F to F_2 ranged from 1:1 to 2:1. With an applied voltage of 27-28 kv., the current output was 55-90 micro-amps. The only products found were fluorocarbons resulting from attack of the F_2 on the Kel-F insulator.

D. Investigations of the Preparation of Derivatives of Chloryl Fluoride

The following studies were carried out in attempts to prepare ionic derivatives of ClO_2F or compounds containing a higher percentage of fluorine than ClO_2F itself.

1/8" Stainless Steel Rod

Kel-F

Gland Nut
Cold Rolled Steel

1 3/4" O. D. Cold
Rolled Steel with
Flats for Tightening

Thrust Washer

Set Screw

To Valve
and Vacuum
System

Recessed Adapter,
Stainless Steel
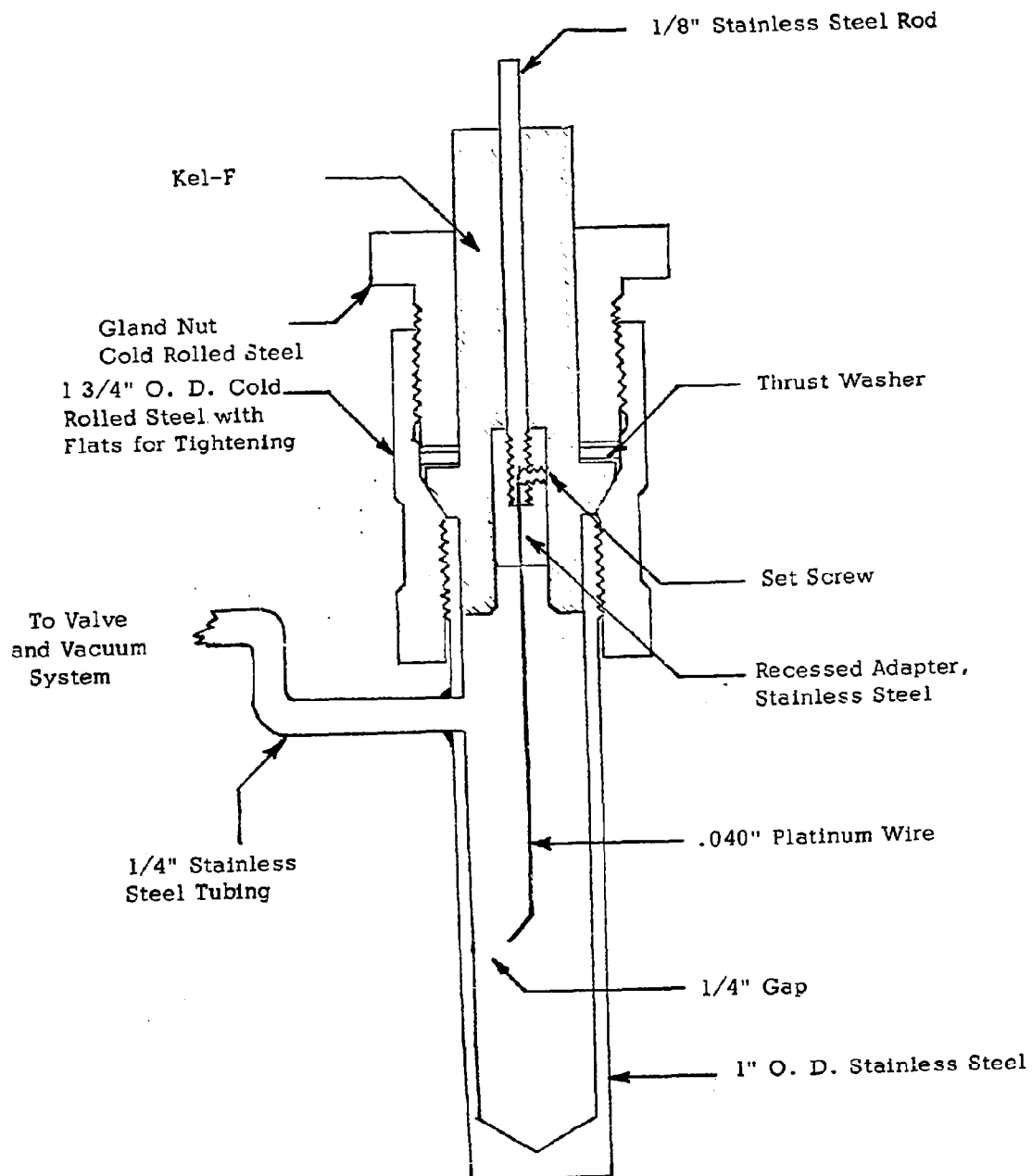
1/4" Stainless
Steel Tubing

.040" Platinum Wire

1/4" Gap

1" O. D. Stainless Steel

Figure 1

Electric Discharge Cell

(Scale Full)

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In our attempts to fluorinate ClO_2F we have used elemental fluorine, chlorine pentafluoride, chlorine trifluoride, cesium tetrafluorochlorate and cesium fluoride as reagents. This work and its results are described below.

The reaction of ClO_2F with an excess of F_2 at temperatures up to 290° resulted in partial conversions (average, about 50%) of ClO_2F to ClO_3F and ClF_5. The overall reaction is considered to be the sum of several independent reactions.

a. $3 ClO_2F \xrightarrow{\Delta} 2 ClO_3F + ClF$

b. $ClF + F_2 \longrightarrow ClF_3$

c. $ClF_3 + F_2 \longrightarrow ClF_5$
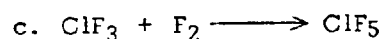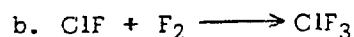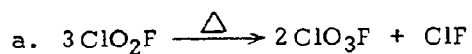
Neither ClF nor ClF_3 was observed in the product gases and Cl_2 and O_2 were also found to be absent.

Mixtures of ClO_2F and ClF_5 when heated to 230°-430° at pressures up to 900 psig resulted in the formation of ClF, F_2, and O_2. The bulk of the ClO_2F was recovered unchanged. The primary reaction appeared to thermal decomposition of ClF_5. It has been determined that pure ClF_5 begins to thermally dissociate at 350°-375° under the experimental conditions used, yielding ClF_3 and F_2.

$$ClF_5 \xrightarrow[1000\,psig]{350-375°} ClF_3 + F_2$$
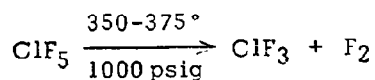
At higher temperatures ($>425°$), dissociation is virtually complete to ClF and F_2.

$$ClF_5 \xrightarrow{\geq 425°} ClF + 2F_2$$
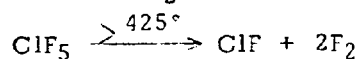
From the results of the experiments with ClO_2F-ClF_5 mixtures, it appears that ClO_2F induces decomposition of ClF_5 to ClF and F_2 at a temperature lower than that required for the pure material.

A complete decomposition of the reactants and a heavy attack on the reactor walls occurred when equimolar amounts of ClO_2F and ClF_3 were reacted at 375°. The volatile products were mainly ClF, Cl_2, and O_2 and the solid residue was a mixture of metal fluorides and chlorides.

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When solid $CsClF_4$ was reacted with gaseous ClO_2F at temperatures up to 300°C in stainless steel cylinders, the products were oxygen, CsF, NiF_2, Cs_2NiF_6 (Ref. 18 and 19), Cl_2, and ClF. Considerable amounts of reactants were recovered unchanged.

In an experiment to attempt either a fluorination of ClO_2F or the formation of the hypothetical salt $CsClO_2F_2$, a mixture of CsF and ClO_2F (3:2 mole ratio) were combined in a monel cylinder and heated to 150° for 28 hours. On cooling, the CsF and ClO_2F were recovered unchanged. Another charge of the CsF and ClO_2F mixture was heated to 300° for 17 hours. On cooling, the gas phase contained only trace quantities of the infrared absorbers CF_4 and SF_6 and the balance of the gas phase was the infrared inactive Cl_2, O_2, and F_2. The recovered yellow solid was subjected to X-ray diffraction analysis, and it has been found to have a pattern similar to CsCl and isomorphous with Cs_2NiF_6.

In subsequent experiments, a number of solid ionic materials postulated to contain the ClO_2^+ ion were prepared by reacting ClO_2F with strong Lewis acids e.g. ClO_2SO_3F, ClO_2SbF_6, ClO_2AsF_6, ClO_2BF_4, and ClO_2PF_6 (Ref. 20 and 21) since complexes of this type offer promise as stable oxidizers providing suitable anions can be combined with the ClO_2^+ moiety. To date such an anion does not exist which forms a stable salt in conjunction with the ClO_2^+ ion.

The alleged preparation of $ClO_2F_2^-$ anions by reaction of chlorates with acid fluoride in aqueous solution has been shown to be in error (see prior discussion). However, it is expected that such an ion would be a strong oxidizer and the preparation would have to be carried out under anhydrous conditions, possibly using materials like ClO_2F as intermediates. Theoretically, the ion is plausible as i would involve an sp^3d bond hybridization which could be described as a trigonal bipyramidal configuration, with the two oxygen atoms and the unshared electron pair in the equatorial position and the two fluorine atoms at the apices.
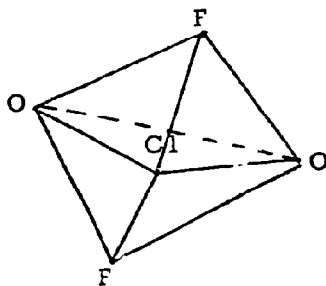
This structure has been postulated for the $IO_2F_2^-$ ion (Ref. 5, page 181) based on X-ray data for the crystal KIO_2F_2 (Ref. 22).

As indicated above unsuccessful attempts to prepare $ClO_2F_2^{-1}$ were made using CsF and ClO_2F as reactants, and subsequent work was carried out using NO_2F and ClO_2F.

An adduct of NO_2F with ClO_2F was prepared by combining the gases and storing the mixture (condensed liquids) at -78° for 4 days. On warming the solid to 0°C the following vapor pressures were noted and plotted on the graph (Fig. 2). The apparatus was not designed for determining the melting point of the solid but it appears to be in the range -30° to -20°C.

Temp. °C	Pressure
-78°	15 mm
-71°	25
-68°	35
-60°	65
-56°	80
-45°	130
-43°	145
-40°	170
-35°	245
-25°	375
-15°	550
-10°	620
-5°	680
0°	740

The plot of the above data shows a discontinuity at $T= -22°C$ which may be attributed to a phase change and is in support of the observed melting point range. More exact pressure data may locate the phase transition with better accuracy.

The $NO_2F \cdot ClO_2F$ solid adduct was treated with ClF_3 to determine the relative stability of the adduct and NO_2ClF_4 (Ref. 23). ClF_3 was condensed on the pale yellow solid at -78°. On warming to about -30°, the adduct appeared to melt and formed an oily layer above the ClF_3. It was found that all three components could be distilled from the two phase system. It would appear that $NO_2F \cdot ClO_2F$ is insoluble in ClF_3.
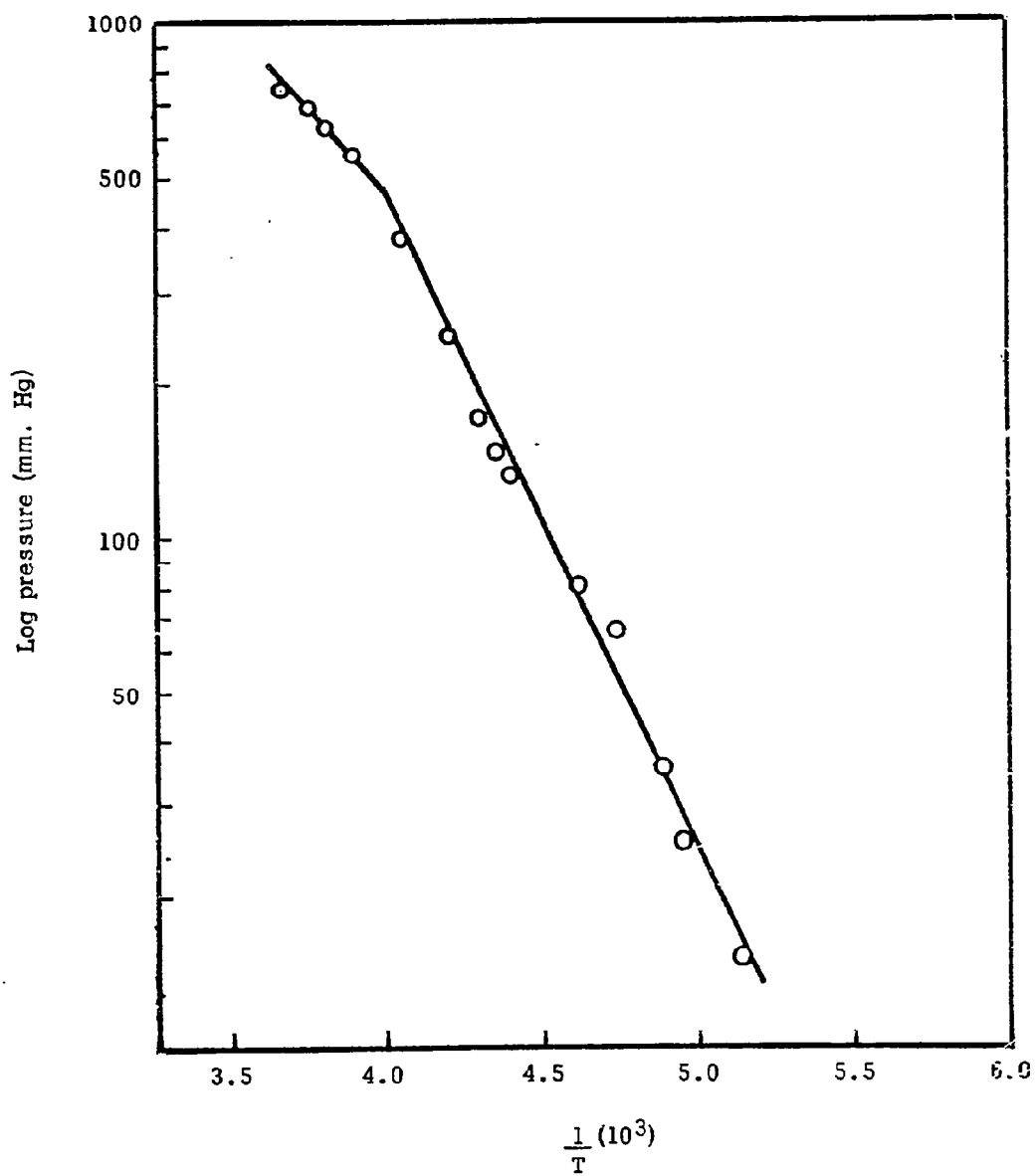
Fig. 2. Vapor pressure of the NO_2F-ClO_2F solid adduct
(Intersection at T=-22° C)

In a second related experiment $NO_2F \cdot ClO_2F$ and an equimolar amount of ClF_3 were heated to 300°C for 10 hours in a large excess of fluorine (10 x). The resulting products were primarily ClF_5 and some ClO_3F, ClO_2F, O_2 and N_2.

E. Investigations of the Preparation of Derivatives of Chlorine Trifluoride

1. A number of exploratory reactions were carried out to determine whether the fluorination of ClF_3 or a physical activation of the ClF_3 molecule could be used — a. to prepare higher fluorinated homologs; b. to effect polymolecular condensations; c. to prepare new ionic Cl-F compounds. Although qualitative considerations of possible valence bond orbital hybridizations, effective atom radii, and orbital energies tend to rule out homologs higher than ClF_5, serious effort was given to this work. The experiments are described below.

Chlorine trifluoride was heated at 470° in an attempt to pyrolyze the material and to condense it to higher homologs; however, this did not occur and the ClF_3 was essentially recovered unchanged.

Continuous discharges of 27,000 volts were placed through pure ClF_3 held at 6-8 psig in the apparatus illustrated in Fig. 2 for periods up to 24 hours. The only products observed were various volatile fluorocarbons resulting fr n attack of the Kel-F insulator by the ClF_3.

In a similar experiment continuous electric discharges (25,000-30,000 volts through mixtures of ClF_3 and F_2 did not appear to cause any reaction at ambient temperature and the reaction times and reactant ratios were varied with no effect. As expected, the potential drop and current flow are dependent on the pressure which was varied in the experiments up to a maximum of 50 psig. Temperature appeared to be the most important variable. At 0° some ClF_5 was formed although the yield was less than 1%; however, on decreasing the temperature to -78°, the amount of ClF_5 is increased five-fold to about 5%.

Apparently the chilled cell is more efficient since the formation of ClF_5 occurs in the liquid phase or at the gas-liquid interface by reaction of fluorine atoms with ClF_3. Since the ClF_5 is in the liquid phase, it is essentially removed from the discharge zone in the gaseous phase and the probability of dissociation is minimized. It is suggested that the mechanism may involve the following reactions:

$$F_2 + e \longrightarrow F^- + F$$

$$F^- + ClF_3 \longrightarrow ClF_4^-$$

$$ClF_4^- + F \longrightarrow ClF_5 + e$$
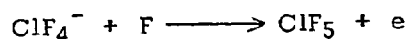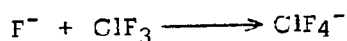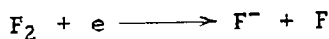
ClF_3 at a pressure of 400 mm. Hg was unaffected by a two hour exposure to a Co^{60} gamma irradiation (240,000 roentgens/hour).

Chlorine trifluoride was reacted with CsF at 80°C and 150 psig for 24 hours to form $CsClF_4$. The reactor was cooled and varying amounts of oxygen were introduced to the reactor. The gas-solid mixture was heated up to 300° developing pressures of up to 3150 psig. The only products observed were ClF and F_2 resulting from decomposition of the $CsClF_4$.

2. A more intense investigation was carried out to prepare oxygenated derivatives of ClF_3. Theoretically it should be possible to prepare $O \leftarrow ClF_3$ and O_2ClF_3 (considered to be distinct from the isomeric unstable adduct reported by Streng and Grosse (Ref. 24) which was prepared by a low temperature reaction of O_2F_2 with ClF). In fact, the former compound has been prepared in this laboratory by the fluorination of Cl_2O and also by the reaction of Cl_2O with OF_2. Rocketdyne had earlier reported the synthesis of $OClF_3$ by the fluorination of Cl_2O and $ClNO_3$ (Ref. 25). This work will be discussed later in the section on "Chlorine Oxides"; it should be noted that all pertinent physical data have not been determined as of this date; however, it is expected that $OClF_3$ will be a relatively stable liquid (extrapolated boiling point, about 30°C). Its structure will probably involve a p^3s hybridization and be tetrahedral; however, since the hybridization will include the 3 p and 4 s orbitals (the latter has lower energy than the 3 d orbital) the configuration may be that of a distorted tetrahedron with the oxygen atom located at stretched apex.
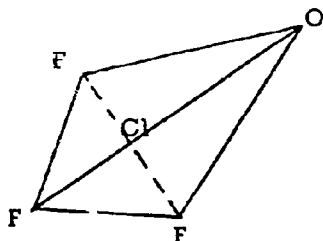
FIGURE 3

CORONA ELECTRIC DISCHARGE APPARATUS
(Sectional Diagram – No scale)
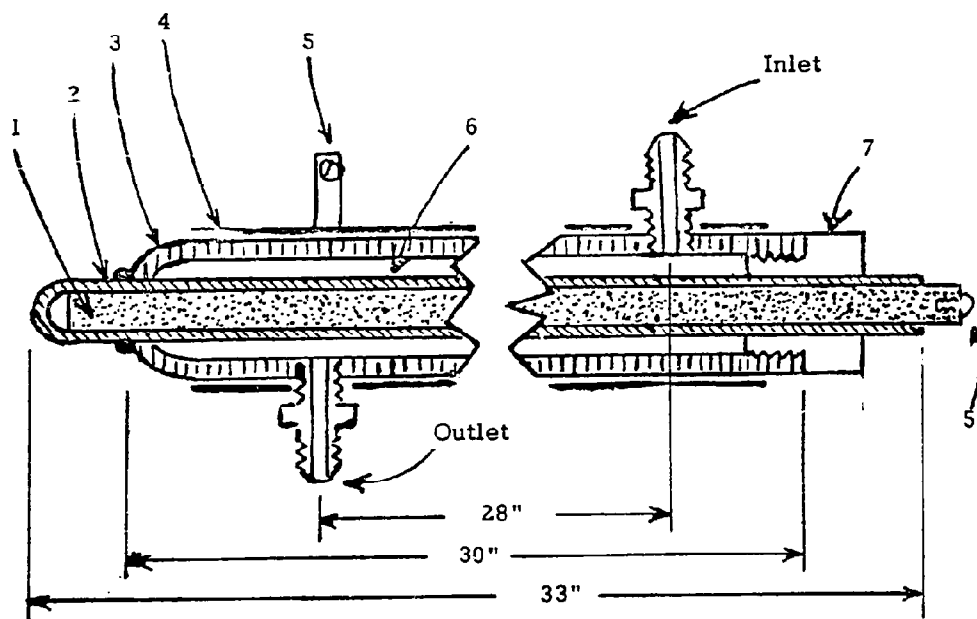
1. Aluminum rod 1/4" D
2. Kel-F tube 3/8" O.D. x 1/4" J.D.
3. Kel-F tube 7/8" O.D. x 5/8" J.D.; ring-seal welded to 2.
4. Aluminum foil covering
5. Electrode connections
6. Annular ring, approx. 1/8" wall-to-wall
7. Threaded Teflon plug
   Inlet and outlet fittings – standard flare fittings (Teflon)

Chlorine trifluoride was combined with CsF to form $CsClF_4$ and this solid material was treated with oxygen at 280-310° at pressures up to 4300 psig in a monel reactor. The only reaction noted was dissociation of $CsClF_4$ to CsF and ClF_3 and subsequently the ClF_3 decomposed to ClF and F_2.

Other reactions which can be considered as attempts to oxidize ClF_3 with ClO_3F and ClO_2F have been described in previous sections which discuss the fluorination of the latter two compounds.

3. During the course of the work studies were made of the known complexes formed by ClF_3 for background information to similar work carried out with ClF_5 and systems investigated in the electrochemical work (see later discussion). Most of the complexes of ClF_3 are ionic and contain either the ClF_2^+ or the ClF_4^- ions.

ClF_2SbF_6 was prepared by combining ClF_3 with SbF_5 (Ref. 26). The reaction is exothermic as evidenced by the warming of the Kel-F trap at the interface of the two reactants and the necessary diffusion of liquid ClF_3 through the solid ClF_2SbF_6 to contact fresh SbF_5 is a convenient rate governing phenomenon; otherwise, the exothermic reaction might have to be controlled by cooling. The density of ClF_2SbF_6 is somewhat between that of SbF_5 and ClF_3 and was tentatively taken as 2.2 g/cc. and the melting point was determined as 225-228°C.

In contrast to the reported unsuccessful attempt to prepare NO_2ClF_4 (Ref. 27) in the open literature, this compound was easily prepared by reacting NO_2F with ClF_3.

It is important to note that in contrast to $NOClF_4$ which is formed on contact of NOF with ClF_3, the formation of NO_2ClF_4 is a slow reaction at -78°. Following preparation of NO_2ClF_4 the vapor pressures were redetermined.

Vapor Pressure of NO_2ClF_4

T (° C)	Observed (mm.)	Calc'd. (mm.)
-50	30, 35	33
-40	65	63
-30	110	111
-20	180	188
-10	300	319
0	490	491
9.5	760	755
15	930, 940	920
20	1120	1122
25	1350, 1360	1369

A least mean square treatment of the above experimental data gave the following equation which was used to determine the calculated values above.

(1) $\log p \text{ (mm)} = 7.945 - \dfrac{1436}{T}$

From these data one may calculate the temperature variation of the equilibrium constant of the dissociation reaction of the following reaction:

(2) $NO_2ClF_4 \text{ (s)} \longrightarrow NO_2F \text{ (g)} + ClF_3 \text{ (g)}$
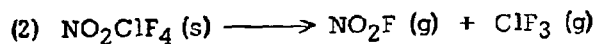
$$Kp = p_{NO_2F} p_{ClF_3} = (1/2 P_{total})^2 = 1/4\, P^2_{total}$$

(P is expressed in atm.)

From the data the following values for the equilibrium constant were determined:

<p style="text-align:center">Temperature Variation of the Equilibrium
Constant for NO_2ClF_4</p>

T° C	Kp (atm.)	log Kp
-50	5.302×10^{-4}	-3.314
-40	1.828×10^{-3}	-2.746
-30	5.237×10^{-3}	-2.264
-20	1.402×10^{-2}	-1.809
-10	3.895×10^{-2}	-1.355
0	0.1039	- .9855
9.5	0.2500	- .6163
+15	0.3824	- .4459
+20	0.5429	- .2755
+25	0.8006	- .1051

These data may be expressed by the following equation:

(3) $\log K_p = 9.409 - \dfrac{2840}{T}$

Assuming that ΔH is invariant with temperature and is represented by the slope of equation (3), one may obtain an approximation of the heat of dissociation of NO_2ClF_4.

$$\frac{-\triangle H}{2.303R} = -2840$$

$\triangle H$ dissociation $= 13$ kcal/mole

The reaction of Na_2O_2 with $CsClF_4$ was carried out in an attempt to introduce oxygen into either the tetrafluorochlorate anion or the ClF_3 molecule, e.g.

$$CsClF_4 + Na_2O_2 \longrightarrow CsClO_2F_2 + 2NaF$$

$$2CsClF_4 + 3Na_2O_2 \longrightarrow 2CsClO_3F + 6NaF$$

$$3CsClF_4 + Na_2O_2 \longrightarrow 3CsF + 2NaF + ClF + 2OClF_3$$

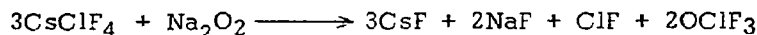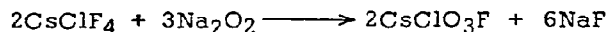From $-78°C$ up to $300°C$ only a trace of reaction was noted with ClO_2F, ClF and O_2 being the only products. When a separate mixture was programmed for a heating period at $400°C$, an exothermic reaction seemed to be initiated within 30-35 minutes of the start of heating or when the temperature reached about $315°C$. The reaction then appeared to be sustained and exothermic. Within the hour the reaction appeared to be finished and heating an additional 6 hrs. produced no changes. The reaction products were chiefly O_2 and Cl_2 plus a solid mixture containing CsF, NaF, $CsClF_4$, and a small amount of Cs_2NiF_6.

In a similar approach, the reaction of Na_2O_2 with ClF_2SbF_6 was carried out in an attempt to bring about the following reaction:

$$Na_2O_2 + ClF_2SbF_6 \longrightarrow ClOF + NaF + NaSbF_6 + 1/2 O_2$$
or
$$Na_2O_2 + ClF_2SbF_6 \longrightarrow ClOF_3 + SbF_3 + 2NaF + 1/2 O_2$$
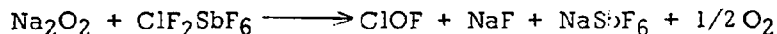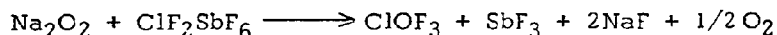
The Na_2O_2-ClF_2SbF_6 system was less reactive than the Na_2O_2-ClF_4SbF_6 system (see Section F). No appreciable reaction was noted up to $125°C$ and the conversion, after 24 hours, was only 2-4% at $160°-170°C$. At $250°C$, a sudden reaction occurred after a delay of about 30 min. at $250°C$ and a temperature rise of $30°C$ at the wall of the autoclave was noted in less than one minute. On cooling, the products were found to be ClF_3, ClF, ClO_2F and O_2 and the solid product was $NaSbF_6$. At $250°C$, the reaction was 90-95% complete (estimate based on recoveries). No new or unknown compounds were detected.

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F. Investigations of the Preparation of Derivatives of Chlorine Pentafluoride

The approach to the preparation of derivatives of ClF_5 was similar to that used for ClF_3 and broadly, can be grouped under three headings: (1) attempts to form other Cl-F compounds, (2) attempts to prepare Cl-O-F compounds and (3) attempts to incorporate the ClF_5 molecule in an adduct or salt useful as a solid oxidizer.

Two preparative methods for ClF_5 were used and their relative merits were compared. The first method involved the following separate reactions:

$$CsF + ClF_3 \xrightarrow[\text{150 psig}]{80°} CsClF_4$$

$$F_2 + CsClF_4 \xrightarrow[\text{1300 psig}]{150°} ClF_5 + CsF$$
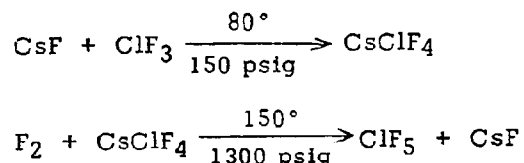
The above sequence usually required three days per batch of ClF_5 (10-15 grams) with conversions of 60-85%. Yields based on the $CsClF_4$ converted were nearly 100%.

The second method was a direct fluorination of ClF_3:

$$F_2 + ClF_3 \xrightarrow[\text{2500 psig}]{300°}$$
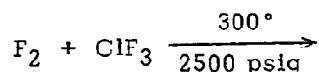
In contrast to the first procedure, the direct fluorination is the better method for laboratory preparation since it only requires one day per batch and conversions of ClF_3 are above 90%. Yields of over 100 grams of ClF_5 are usually obtained in a single run using a conventional laboratory scale autoclave.

It was found that the latter preparative method was sensitive to the composition of the reactor metal with the best yields obtained in nickel. Under conditions producing near quantitative yields in nickel reactors, experiments carried out in stainless steel or monel reactors gave either much less ClF_5 or no ClF_5 at all.

As in the case of ClF_3, attempts to prepare novel Cl-F compounds using ClF_5 as an intermediate have involved pyrolysis, fluorination and electric discharge techniques.

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Pyrolyses of ClF_5 were attempted at 375° and 430° to determine whether ClF_5 could be condensed to higher homologs or to solid material. At 375° in a nickel reactor (maximum pressure, 500 psig), ClF_5 decomposed only slightly ($\leq$ 10%) to ClF_3 and F_2. At 430° in a monel reactor, ClF_5 was quantitatively decomposed to ClF_3, ClF, and F_2. Note again the apparent effect of the reactor metal.

An attempt to upgrade ClF_5 with elemental fluorine was unsuccessful. A 4:1 mixture of F_2 and ClF_5 was heated to 375° for 16 hours with a maximum pressure of 2800 psig. The only observed reaction was a decomposition of ClF_5 to ClF_3. This was unexpected in view of the large excess of fluorine present in the reactor.

ClF_5 did not form an adduct with, or react with, CsF in a liquid-solid phase reaction at -78° for 8 days. The same reactants were transferred to an autoclave and the system was heated to 150°. This was followed by a reaction with a second mixture at 300°. Material balances were obtained in both cases as shown below.

	Reaction Temperature			
	150°		300°	
CsF charged (moles)	0.10		0.10	
ClF_5 charged	0.12		0.12	
ClF_5 recovered	0.054		0.047	
ClF_5 consumed		.068		.073
F_2 recovered		.071		.097*

(* probably a small quantity of air in recovered sample)

X-ray diffraction analysis indicates that the solid products are mixtures of $CsClF_4$ and CsF. The overall reaction can be summarized by the following equations:

a. $ClF_5 \longrightarrow ClF_3 + F_2$

b. $ClF_3 + CsF \longrightarrow CsClF_4$
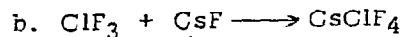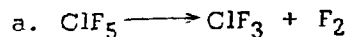
In other experiments pure ClF_5 and mixtures of ClF_5 with ClF_3 were subjected to electric discharges of 19,000 to 30,000 volts at pressures of 532 mm. Hg to 20 psig in attempts to upgrade the fluorine content of the ClF_5 or to form new chlorine fluorides. No new products were observed.

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As is pointed out in the Introduction to this report, the structure of ClF_5 is considered to be similar to that of BrF_5 — i.e. octahedral with the unshared electron pair occupying one corner.
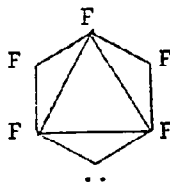
Under the proper conditions, it might be expected that the electron pair could form a dative bond with certain electron deficient atoms or molecules as O, NO, NOF, etc. Typical of these would be ClF_5O and this compound might still retain the octahedral configuration of the original ClF_5.

In addition, the pyrolytic degradation of ClF_5 or degradation of ClF_5 by physical means may produce intermediates more reactive toward oxygen-containing reagents than either ClF_5 or ClF_3.

The following experiments were carried out to form novel Cl-O-F oxidizers.

Chlorine pentafluoride and O_2 were reacted together, in two separate experiments, at 375° and 430°. A 7:1 mixture of O_2 and ClF_5 is stable indefinitely at 25°; however, when the mixture was heated to 430° for 16 hours (maximum pressure, 2600 psig) the ClF_5 decomposed completely to ClF_3 and F_2. At 375°, the decomposition of ClF_5 was only slight under the same conditions. It appears that oxygen has no effect on the thermal stability of ClF_5.

Gaseous ozone, generated by a Welsbach unit, was passed through ClF_5 maintained at -95° to -97°C. There was no visible reaction and no new products were formed. When ozone was passed through a solution of ClF_5 in CCl_2F_2 at -80° the products were ClO_3F, ClO_2F, and ClF_3.

Equimolar mixtures of gaseous ClO_2F and ClF_5 were heated to 260°C and little or no reaction occurred. However, at 420° only residual traces of ClO_2F and ClF_5 could be detected. There were no solid products and the bulk of the gaseous products were non-absorbing in the infrared region of 2-15 microns indicating

decomposition of the reactants to the elements. This reaction was discussed in detail in the section concerned with the chemistry of ClO_2F. Equimolar amounts of ClF_5 and ClO_3F did not react at 300°C; therefore, the temperature was increased to 400°C. It was expected that ClF_5 would decompose; however, it was hoped that the ClO_3F might react with any transient intermediates or radicals associated with the ClF_5 decomposition. This was not the case and the only products observed were ClF, ClF_3, ClO_3F and F_2. There was no indication of the formation of the hypothetical ClO_3ClF_6 or the simpler derivative ClF_5O.

A similar experiment using F_2 as a pressurizing gas (310°C; 2600 psig) was also unsuccessful and the ClO_3F and ClF_5 were recovered unreacted.

A 20% mole excess of NO_2F was reacted with ClF_5 at -78°C for several days. The excess NO_2F was easily removed under vacuum (vapor pressure of NO_2F, 560 mm at -78°; ClF_5, 23.6 mm). The residual material at -78° was a relatively non-volatile yellow liquid with a vapor pressure of about 5 mm Hg, containing 4.1 g. (0.063 moles) of NO_2F and 8.7 g. (0.067 moles) of ClF_5. The mole ratio ClF_5/NO_2F is 1.06 indicating an equimolar complex.

$$NO_2F + ClF_5 \longrightarrow NO_2F \cdot ClF_5$$
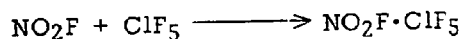
On warming the complex to -35° (v.p. 310 mm) both NO_2F and ClF_5 can be identified in the vapor phase by infrared analysis.

It is interesting to note that the liquid material cannot be a simple solution since the vapor pressure (5 mm Hg) at -78° is considerably less than that predicted by Raoult's Law

$$P_T = \sum_{0}^{i} x_i P_i = .5 \times P_{ClF_5} + .5 P_{NO_2F} =$$

$$.5 \times 23.6 + .5 \times 560 = 291.8 \text{ mm}$$

The observed vapor pressure of the adduct is given below and is presented graphically in Fig. 4.

- 29 -

Vapor Pressure of the $NO_2F \cdot ClF_5$ System

Temp (°C)	Pressure (mm Hg)
-105	5
-100	10
-95	15
-90	25
-85	35
-78	55
-70	90
-65	130,135
-60	155
-55	230
-50	275
-45	365
-42	385
-40	420
-35	560,570
-30	685
-28	760
-25	840,850
-20	1045
-15	1210
-10	1510

In contrast to the solid adduct formed by NO_2F and ClF_3, the NO_2F-ClF_5 system produces a liquid which likely is a molecular adduct rather than a polar complex.

Quantities of ClF_2SbF_6 and ClF_4SbF_6 were synthesized by reactions of SbF_5 with ClF_3 and ClF_5. Neither solid had an appreciable vapor pressure (i.e. greater than 5 mm) at 25°. Although reactions have been carried out using excesses of both SbF_5 and ClF_5, we have found only a single well-defined combining ratio of 1 mole ClF_5 to 1 mole SbF_5. This is in contrast to data obtained by other investigators (Ref. 28) who report ratios of 2.5-1.5 SbF_5 to 1. ClF_5. This is probably associated with the difficulties of assuring complete reaction and removing unreacted starting materials. Reaction at -14° (b.p. of ClF_5) is complicated by the fact that SbF_5 (m.p. 7°C) is frozen and the ClF_5 must diffuse through the ClF_4SbF_6 formed before it can contact and react with the solid SbF_5. At ambient temperature the liquid SbF_5 wets the product and reaction between gaseous ClF_5 and liquid SbF_5 proceeds rapidly. Due to the low vapor pressure of SbF_5 (b.p. 143-145°) it is preferred to use a large excess of ClF_5.
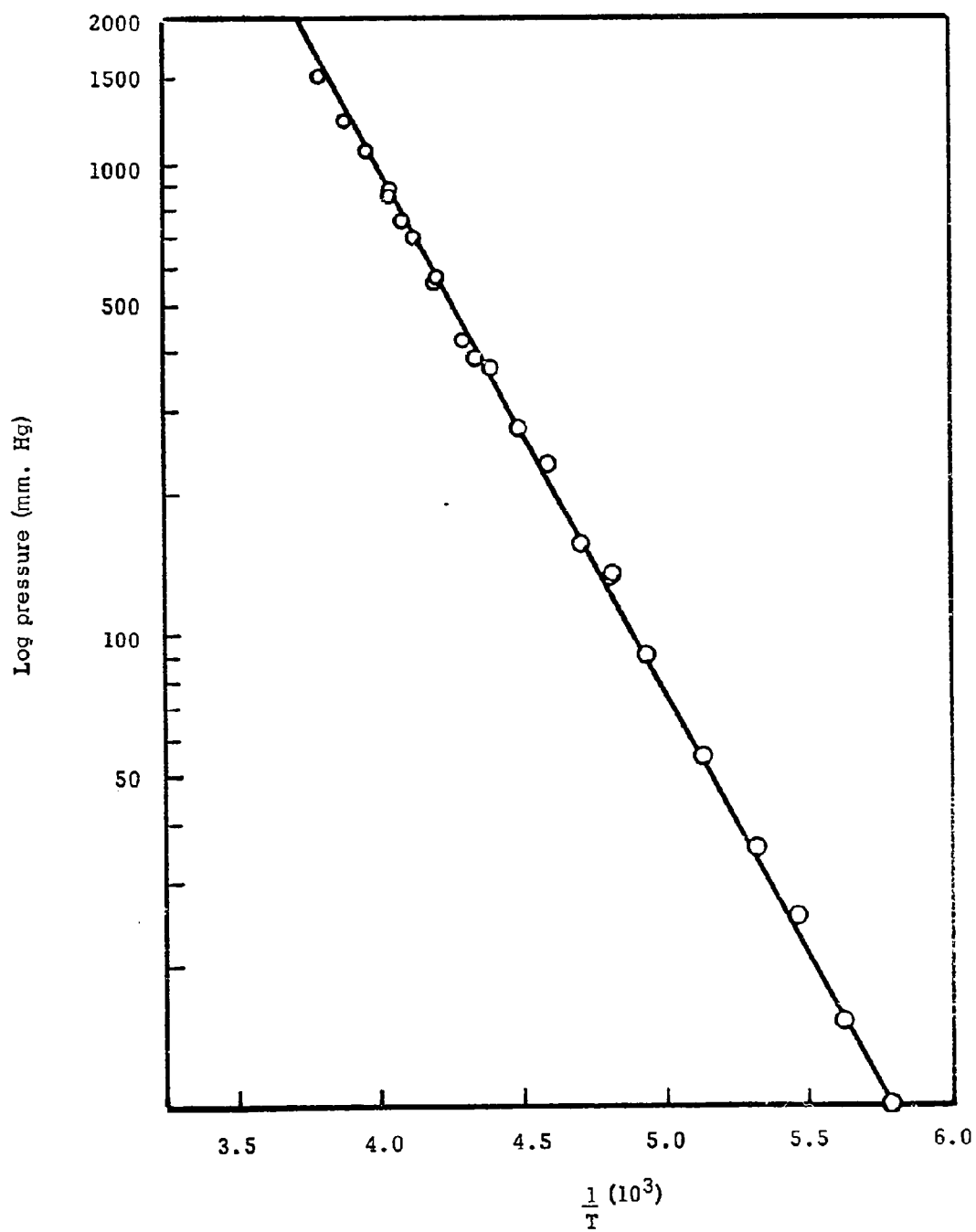
- 30 -

Fig. 4. Vapor pressure of the NO_2F-ClF_5 System

- 31 -

The melting points were determined as 34-35° for ClF_4SbF_6 and 225-228° for ClF_2SbF_6. In charging X-ray sample tubes the ClF_4SbF_6 will melt due to the warmth of the technician's hand. Loading was easily carried out by chilling the sample beforehand and by cooling the fingers of the dry-box gloves prior to handling the sample tube.

X-ray diffraction patterns have been obtained for both ClF_2SbF_6 and ClF_4SbF_6; however, the resolution is not of high quality.

Attempts have been made to obtain infrared absorption spectra of these materials by the use of mulls with perfluorinated solvents or by pelleting the samples with inorganic diluents. These salts are so reactive that only highly fluorinated solvents are compatible and the fluorinated solvents on hand are either so volatile that a poor mull results (through evaporation of the solvent and subsequent light scattering and diffraction) or the solvents have an excessive infrared absorption of their own.

Both ClF_2SbF_6 and ClF_4SbF_6 were compatible with FC-75 (Minnesota Mining and Manufacturing Company perfluorinated cyclic ether), fluorolube oils, and Halocarbon Oil 11-21. With Kel-F Oil #10, the solids turned red and some coloration was imparted to the oil. There is smoke, charring, and fire when the solids are contacted with CCl_4, I-113 ($CFCl_2CF_2Cl$), $CHCl_3$, silicone oils, mineral oils, fluorobenzene, chlorobenzene, toluene and benzene.

The extreme reactivity of these salts is indicated in Fig. 5. The botton sections of an electrochemical cell are shown. These are fabricated of Kel-F plastic which is inert to ClF_3, ClF_5, and SbF_5 at 25°. However, on contact with either ClF_2SbF_6 or ClF_4SbF_6 for 6-10 hours at 25° severe stress cracking results. It is emphasized that these cracks are not due to thermal strains and have been observed also in Kel-F bottles used to store the solids. It is believed that extreme fluorination of the plastic occurs locally due to the reactivity of ClF_2^+ and ClF_4^+ cations which causes surface stresses eventually leading to cracks. In general, the ClF_4^+ appears to be more reactive than ClF_2^+ and will produce the cracking phenomena in about half the time.
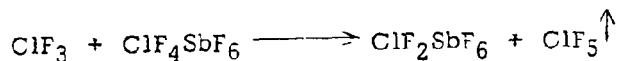
It was observed that, when ClF_3 was added to solid ClF_4SbF_6, the material will slowly dissolve and simultaneously evolve ClF_5. It is believed that a displacement occurs according to the following equation:

- 32 -

Fig. 5
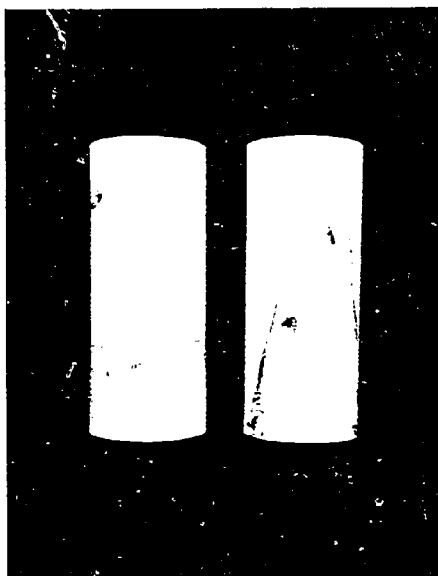
Stress Cracked Kel-F Plastic. Result of
Contact with ClF_5-SbF_5 Adduct. (Cracks
treated with dye for contrast).

$$ClF_3 + ClF_4SbF_6 \longrightarrow ClF_2SbF_6 + ClF_5 \uparrow$$

The solid ClF_4SbF_6 dissolved in SbF_5 was heated to 375° in a stainless steel autoclave. The mixture decomposed completely and severely corroded the autoclave to produce metal fluorides and chlorides. A residual pressure of 570 mm. Hg. was due to the unexplained presence of CF_4, C_2F_6, and SiF_4.
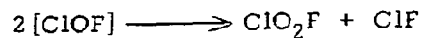
ClF_5 was reacted separately with SF_4, SF_6, and BF_3 at 25° and pressures up to 40 psig. There was no indication of the formation of complexes. The systems were then cooled to -78' and still no evidence for complex formation was obtained.

ClF_5 and $KClO_3$ reacted to a very slight extent at 150°C yielding small amounts of ClO_3F and OF_2 in the vapor phase and a detectable quantity of KF in the solid. However, at 250°C, the reaction was nearly complete since only _traces_ of residual ClF_5 could be detected. The major components of the gaseous products were ClO_3F and ClO_2F with lesser amounts of O_2 and OF_2. The X-ray diffraction pattern of the residual solid was identical to that reported for $KClF_4$ (Ref. 29).

ClF_5 and $KClO_4$ reacted slightly at 150° to give traces of O_2, ClO_3F, and ClO_2F and some KF in the solid. At 250°C reaction was substantially greater producing ClO_3F and O_2 as the major volatile products along with a lesser amount of ClO_2F and some residual ClF_5. X-ray powder pattern of the solid showed primarily KF and KHF_2 with additional lines which coincide with the major lines listed for $KClF_4$ (see ref. above).

Similar work was carried out using $CsClO_4$ as a reactant and the volatile products were identical to those obtained using $KClO_4$. The solids were CsF, $CsHF_2$, and some $CsClF_4$.

The controlled hydrolyses of ClF_3 and XeF_6 yield, respectively, ClO_2F and $XeOF_4$. The probable reactions may be as follows:

$$ClF_3 + H_2O \longrightarrow [ClOF] + 2HF$$

$$2[ClOF] \longrightarrow ClO_2F + ClF$$

and

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
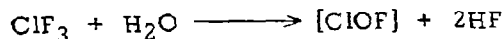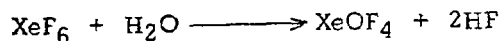
By analogy, ClF_5 might react with water under moderated conditions to yield $OClF_3$.

$$ClF_5 + H_2O \longrightarrow OClF_3 + 2HF$$
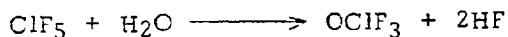
Since direct hydrolysis is difficult to control, the water was used in the form of a hydrate of nickel fluoride and the reaction was studied in both static and flow systems.

static system:

A mixture of $NiF_2 \cdot 4H_2O$ and ClF_5 was reacted overnight with heating (200°). In addition to the unused excess ClF_5, the gaseous products obtained were primarily ClO_2F and ClO_3F, with some HF. The concentration of ClO_2F was slightly higher than that of ClO_3F. The solid phase contained NiF_2 and $NiF_2 \cdot xHF$. The overall reaction may be represented by two competing reactions:

$$2ClF_5 + NiF_2 \cdot 4H_2O \longrightarrow 2ClO_2F + 8HF + NiF_2$$

$$4ClF_5 + 3NiF_2 \cdot 4H_2O \longrightarrow 4ClO_3F + 16HF + 3NiF_2 + 4H_2$$

flow system:

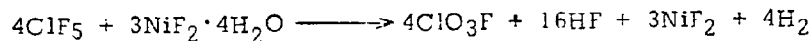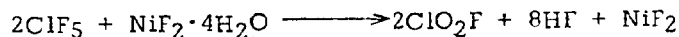ClF_5 was passed over $NiF_2 \cdot 4H_2O$ in a monel tube in two experiments at ambient temperature and at 190° for a total of 3.5 hours each. The only products observed were principally ClO_3F and some ClO_2F. The solid residue contained NiF_2, $NiF_2 \cdot 4H_2O$, and some lower hydrates. These results plus those above indicate that a static system favors the formation of ClO_2F and a flow system favors ClO_3F. In addition higher temperatures in the flow system yield larger quantities of ClO_2F. These data are opposed to the expected results if one proposes the formation of ClO_3F by the thermal decomposition of ClO_2F.

In a subsequent brief exploratory reaction carried out for background information, a mixture of ClF_5 and SiO_2 was heated slowly to 250° with no sign of reaction. After 1.3 hours at 250° a a sudden exothermic reaction occurred, and the pressure went from an autogeneous 600 psig to an unknown peak pressure and returned finally to 1850 psig within minutes. Considering the mass of the autoclave the heat liberated must have been appreciable to give such a fast response to the temperature rise. The thermocouple was located in the autoclave wall and is normally slow to

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respond to thermal changes. On cooling the products were found to be SiF_4, ClF_3, O_2, some ClO_2F, and a trace of unreacted ClF_5.

The synthesis of novel Cl-O-F compounds was attempted using Na_2O_2 to introduce oxygen into the halogen fluorides and their derived ions.

Possible reactions might be:

$$Na_2O_2 + ClF_5 \longrightarrow ClO_2F_3 + 2NaF$$

$$Na_2O_2 + 2ClF_5 \longrightarrow 2ClOF_3 + F_2 + 2NaF$$

$$Na_2O_2 + 2ClF_5 \longrightarrow ClOF_3 + ClOF_5 + 2NaF$$
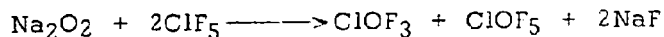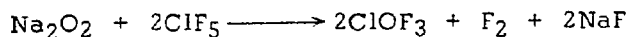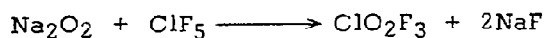
No reaction was detected at 25 °C but on increasing the temperature a sudden vigorous exothermic reaction occurred at 150° which appeared to be initially a thermal decomposition of the Na_2O_2 followed by reaction of the Na_2O_2 and its degradation products with ClF_5 to form NaF and ClF_3. The heat was sufficiently intense to decompose most of the ClF_5 to ClF_3 and a small amount of ClF.

The reaction of Na_2O_2 with ClF_4SbF_6 was studied in an attempt to introduce oxygen into the ClF_4^+ cation. The synthesis of $ClOF_3$ and/or $ClOF_5$ might be realized from a reaction of this type according to the equation:

$$Na_2O_2 + ClF_4SbF_6 \longrightarrow ClOF_3 + NaF + NaSbF_6 + 1/2 O_2$$
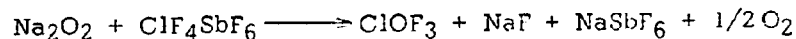
a 2:1 molar mixture of ClF_4SbF_6:Na_2O_2 was subjected to slow stepwise heating from -78°C to 250°C. The above proposed reaction did not take place; however, known compounds such as ClO_2F, ClF_5, ClF_3, ClO_3F and some O_2 were obtained as the volatile products. The solid product was $NaSbF_6$, as expected. The reaction was slow and the conversions, after 24 hours, were as follows: 2-4% at 75°C, 10-15% at 125°C, 30% at 160-170°C and 30% at 250°C. Additional time would undoubtedly have brought the reaction to completion.

G. Investigations of the Fluorination of Chlorine Oxides

As discussed previously, it has been proposed that compounds and ions such as $OClF_3$, O_2ClF_3, $OClF_5$, $O_2ClF_2^-$,

$OClF_2^+$, etc., may be sufficiently stable to be isolated and studied. This phase of the work was an attempt to prepare these compounds and ions by the fluorination of the unstable, explosive, odd-electron molecule ClO_2 or the analogous, more stable, Cl_2O.

ClO_2, diluted with nitrogen, reacted completely with ClF_5 at a maximum temperature of 110° to produce ClO_2F and Cl_2 which were identified by infrared and mass spectrometric analysis. With the exception of the excess ClF_5, no other products were detected. The reaction might be represented by the following overall equation:

$$10\,ClO_2 + 2\,ClF_5 \longrightarrow 10\,ClO_2F + Cl_2$$
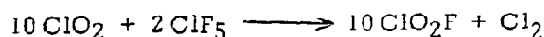
The results indicate that all of the fluorine in ClF_5 enters into the reaction and that ClF_3 and ClF (the degradation products of ClF_5) would probably behave in an analogous way.

No reaction occurred between NF_3 and ClO_2 under flow conditions at ambient pressure and temperature up to 110°C.

OF_2 is a strong oxidizer and it was considered probable that it might serve as a fluorinating agent toward ClO_2 under flow conditions at moderate temperatures ($\leq$ 110°C). The product mixture contained primarily ClF_5, a significant amount of ClO_2F and a lesser amount of ClO_3F. It is suspected that O_2 was also formed; however, no specific attempt was made to trap or isolate it. The following equations probably represent only a few of the many possible reactions which occur:

a. $4ClO_2 + 6OF_2 \longrightarrow 2ClF_5 + 5O_2 + 2ClO_2F$

b. $2ClO_2F + O_2 \longrightarrow 2ClO_3F$

c. $2ClO_2 + F_2 \longrightarrow 2ClO_2F$

d. $ClO_2 + OF_2 \longrightarrow ClO_3F + 1/2\,F_2$

e. $2ClO_2 + OF_2 \longrightarrow ClO_2F + ClO_3F$
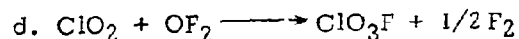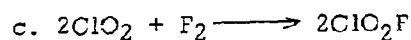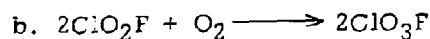
The results would indicate that equation a. represents the general overall reaction and that equation b. occurs to a significant extent. No new or unidentified materials were detected.

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The reaction of ClO_2 with F_2 is the preparative method for the synthesis of ClO_2F. Since N_2F_4 can be considered as a pseudohalogen, readily dissociating to $NF_2 \cdot$ radicals, it is reasonable to suppose that N_2F_4 might react with the odd-molecule $ClO_2 \cdot$ to form ClO_2 as below.
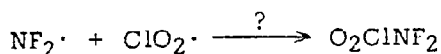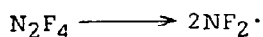
$$N_2F_4 \longrightarrow 2NF_2 \cdot$$

$$NF_2 \cdot \ + \ ClO_2 \cdot \ \xrightarrow{\ ?\ } \ O_2ClNF_2$$

The reaction was smooth and the only products isolated were NOF and Cl_2 as well as small amounts of N_2 or F_2. There was no residual ClO_2 in the product mixture and no new or unknown materials were detected.

The study of the fluorination of Cl_2O was initiated by reacting it with F_2 at ambient temperature in a flow system. Cl_2O was freshly prepared in advance by passing a (1:1) Cl_2/N_2 mixture at about 200 cc/min. (total flow) through a 24" x 1" monel reactor packed with 31.0 g. (0.143 moles) yellow basic HgO on glass wool. The Cl_2O was condensed at -78°C and stored at this temperature until time for use. The red-brown liquid at -78°C was predominantly Cl_2O containing a small amount of unconverted Cl_2.

The crude Cl_2O was warmed from -78°C to 0°C and vaporized with a stream of N_2 passed at a rate of about 250 cc/min. This Cl_2O/N_2 mixture was combined with F_2 (280-300 cc/min.) at ambient temperature and the entire mixture was then passed through a 4000 ml. reactor (estimated residence time; 7 min. $\pm$ 1 min.). The condensable products were caught in a trap cooled with liquid oxygen (-183°). The products were identified as ClO_2F, ClF_3 and some ClO_3F.

Cl_2O and a large excess of F_2 were charged to a monel reactor and kept at 155°C for 7 hrs. at a maximum autogenous pressure of 690 psig. Aside from excess F_2, the product mixture contained ClO_2F and ClF_3 as the major products, ClO_3F and ClF_5 as minor products plus a novel material believed to be ClF_3O. The ClF_3O is still slightly in doubt because of the interference in its infrared absorption spectra by ClO_2F, ClF_3 and the other products and since the material was in small concentrations.

The identification of ClF_3O was aided by the fact that during the time this work was in progress Rocketdyne personnel reported their synthesis of this same compound and its infrared spectrum.

In subsequent experiments, Cl_2O and a large excess of OF_2 were passed through a copper coil reactor at 15-20°C for several hours. No reaction occurred. In a variation of this reaction a 1:3 molar mixture of Cl_2O and OF_2 were heated for 5 hours at 130°C in a monel reactor and no reactor occurred.

This same 1:3 molar mixture of Cl_2O and OF_2 was then heated at 185° for 20 hours (maximum pressure, 1275 psig). (Note thermal decomposition of OF_2 is appreciable in the 200°-220°C range.) After 8 hours reaction the products were condensed and pumped at -78° to remove ClO_3F, ClF_5, ClF_3, and ClO_2F leaving residual pure ClF_3O.

Further work on the preparation and properties of this new oxidizer was not possible since the contract expired.

H. Investigations of the Chemistry of Oxygen Difluoride

A number of reactions were carried out using OF_2 in attempts to introduce either oxygen or the -OF group into ClF_x molecule and other molecules. It was also of interest to investigate the possibility of polarizing the O-F bond and forming complexes of OF_2. A few proposed reactions include:

$$OF_2 + ClF_3 \longrightarrow OClF_5 \text{ or } FOClF_4 \text{ (a covalent hypofluorite)}$$

$$OF_2 + ClO_2F \longrightarrow OF^+ClO_2F_2^-$$

$$OF_2 + ClF \longrightarrow OClF_3$$
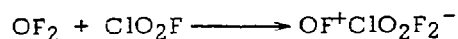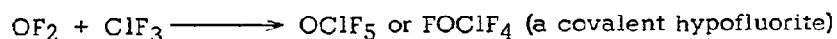
$$\text{etc.}$$

No reaction was detected between OF_2 and ClF_3 at temperatures up to 280°C (macimum pressure, 1350 psig); however, significant thermal decomposition of OF_2 did occur giving O_2 and F_2. The fluorine formed then reacted with the ClF_3 to produce ClF_5. The principal reactions were:

$$OF_2 \longrightarrow 1/2 O_2 + F_2$$

$$F_2 + ClF_3 \longrightarrow ClF_5$$
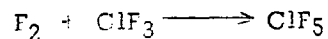
No reaction occurred between OF_2 and ClF_5 at temperatures up to 300° (maximum pressure, 2950 psig). A major portion of the OF_2 was thermally decomposed to O_2 and F_2 and the ClF_5 was recovered quantitatively.

An equimolar mixture of OF_2 and ClO_2F did not react at 250° (maximum pressure, 825 psig). As previously noted at these high temperatures some thermal decomposition occurs. The ClO_2F was recovered along with a small amount of ClO_3F which is believed to be a product of the reaction of oxygen with ClO_2F since ClF and its fluorinated homologs, ClF_3 and ClF_5, were absent. ClF is known to be a product of the thermal dissociation of ClO_2F.

$$3ClO_2F \xrightarrow{heat} 2ClO_3F + ClF$$
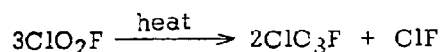
The overall reaction is therefore believed to be a sum of the following reactions:

$$OF_2 \longrightarrow 1/2\, O_2 + F_2$$

$$1/2\, O_2 + ClO_2F \longrightarrow ClO_3F$$
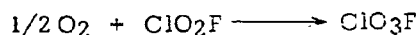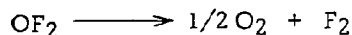
Oxygen difluoride and perchloryl fluoride (ClO_3F) did not react after 20 hours at 200° (maximum observed pressure, 1110 psig). Both compounds were recovered unchanged.

Oxygen difluoride and nitrogen trifluoride did not react after 7 hours at 300° (maximum observed pressure, 1975 psig). Some thermal decomposition of the OF_2 was noted.

Oxygen difluoride and antimony pentafluoride were heated together for 16 hours at temperatures up to 200° (maximum pressure, 760 psig) in an effort to form a complex of the type $OF^+SbF_6^-$ or $O^{++}(SbF_6)_2^=$. However, the reactants were recovered unchanged.

Similarly, OF_2 was reacted with CsF at temperatures up to 200° in the hope of forming a complex. No reaction was noted.

Oxygen difluoride and $CsClF_4$ were combined and heated for 20 hours at 200° (maximum pressure, 790 psig). On cooling, the product gases were found to contain small amounts of O_2, F_2, and ClF_5 which were presumably formed according to the equations.

$$2OF_2 \longrightarrow O_2 + 2F_2$$

$$F_2 + CsClF_4 \longrightarrow CsF + ClF_5$$
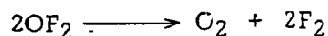
Oxygen difluoride and ClF_4SbF_6 were heated for 18 hours at 200° (maximum pressure observed, 500 psig) and, on cooling, the product gases were found to contain ClF_5, O_2, and F_2 in addition to the residual undecomposed OF_2. Analysis of the remaining solid showed that the ClF_4SbF_6 had decomposed and the residual material was richer in the nonvolatile SbF_5

$$ClF_4SbF_6 \longrightarrow ClF_5 + SbF_5$$
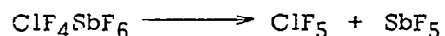
No reaction was detected between OF_2 and ClF_2SbF_6 after 20 hours at 200°C (850 psig). As usual some decomposition of the OF_2 was obtained. Mass spectrometric analysis of the total gas phase indicated the presence of OF_2, O_2 and a small amount of Cl_2 and ClF_5.

Oxygen difluoride reacted with anhydrous CsCl at 200° to produce a mixture of gases including O_2, Cl_2, some ClF and ClO_2F and a small amount of CF_4 and SiF_4 (the latter two compounds were found to be impurities in the particular sample of OF_2 used). The major products were chlorine and oxygen. The residual solid was CsF admixed with a small amount of $CsClF_4$ and sufficient Cs_2NiF_6 to impart a reddish color to the solid. The principal reactions probably include the following:

$$OF_2 + 2CsCl \longrightarrow 1/2 O_2 + Cl_2 + 2CsF$$

$$OF_2 \longrightarrow 1/2 O_2 + F_2$$

$$Cl_2 + 3F_2 \longrightarrow 2ClF_3 \text{ (and ClF in the presence of excess } Cl_2)$$

$$ClF_3 + CsF \longrightarrow CsClF_4$$

$$2ClF_3 + 2CsF + \text{reactor metal} \longrightarrow Cs_2NiF_6 + Cl_2 + MF_2$$
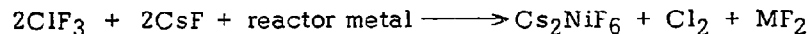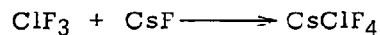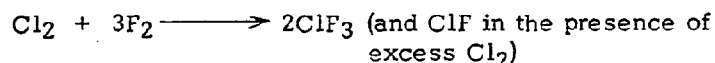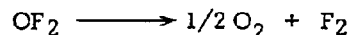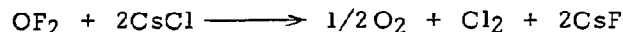
The ClO_2F can be accounted for by the oxidation of ClF.

In order to further explore the reaction of OF_2 with metal chlorides in search of Cl-O-F compounds, OF_2 and NaCl were heated in a monel cylinder at 200°C for 18 hours (maximum pressure, 940 psig). A reaction occurred and 94% of the oxygen in the charged OF_2 was recovered as O_2. In addition the chlorine in the NaCl used was almost quantitatively recovered as Cl_2. Other gaseous products were very small amounts of ClF and ClO_2F as well as CF_4 and SiF_4 present as impurities in the OF_2.

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$$4NaCl + 2OF_2 \longrightarrow 4NaF + 2Cl_2 + O_2$$

Calcium chloride (anhydrous) and OF_2 were charged to a monel cylinder and, following the introduction of the OF_2 at $-196°$, the cylinder was allowed to warm. During the warming period, a sudden and highly exothermic reaction occurred which heated the cylinder to a high temperature. After standing 24 hours, the products in the cooled cylinder were found to be O_2 and Cl_2 with small amounts of ClF, ClF_3, ClO_2F and some unreacted OF_2. The nonvolatile solid residue was identified as CaF_2. The principal reaction was:

$$CaCl_2 + OF_2 \longrightarrow CaF_2 + 1/2 O_2 + Cl_2$$
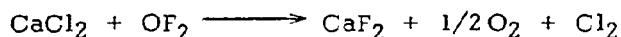
The reaction of OF_2 with Cl_2 was carried out in an attempt to prepare ClOF, $ClOF_3$, $ClOF_5$ or ClO_2F_3. Streng (Ref. 30) stated that when OF_2-Cl_2 mixtures were passed through a copper tube at $300°C$, small explosions occurred. In addition it was reported that on warming mixtures of OF_2 and the halogens Cl_2, Br_2 or I_2, from $-196°C$, explosions occurred.

The mixture of OF_2 with Cl_2 employing N_2 as a diluent, gave indications of a trace of a smooth reaction occurring. Therefore, it was decided to eliminate the N_2 and to conduct the experiment at ambient temperature or above despite Streng's warnings of explosions. A binary mixture of OF_2 and Cl_2 was warmed to ambient temperature but no reaction was observed after 4 days under these conditions. Heating at $150°C$ finally resulted in the formation of ClF and O_2 as principal products. It is suggested that the following reaction occurred:

$$2Cl_2 + 2OF_2 \longrightarrow 4ClF + O_2$$
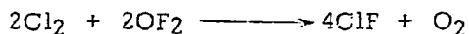
No reaction was detected at ambient temperature between OF_2 and ClF; however, at $150°C$ a slow reaction occurred as indicated by a decrease in pressure over a period of time. The main products in this reaction were ClF_3 and O_2 and a lesser amount of ClO_2F. The predominance of ClF_3 indicates that perhaps two sets of reactions occurred. Although OF_2 by itself is thermally stable to about $200°C$, the decomposition to O_2 and F_2 was presumably initiated or catalyzed by ClF resulting in the following sequence of reactions:

$$2OF_2 \longrightarrow O_2 + 2F_2$$

$$2ClF + 2F_2 \longrightarrow 2ClF_3$$

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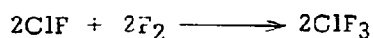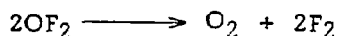
In addition to the ClF_3 was found a small amount of ClO_2F which probably formed through an oxidation of ClF by elemental oxygen.

$$ClF + O_2 \longrightarrow ClO_2F$$
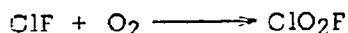
Another attempt was made to react OF_2 with ClF under conditions less severe than described above. The gaseous OF_2 was reacted in a flow system with ClF diluted with N_2 at a 4-6 minute residence time. In addition to the recovered reactants, the product mixture contained some O_2 and another unidentified component(s). The unknown materials were present in very small amounts and possessed infrared absorptions bands in the regions of 5.40, 6.15, 7.45, 7.8-7.9, 8.92, 9.55, and 11.8μ. Mass spectrometric patterns of the unknown materials gave a pattern which indicated that our sample reacted with the tube walls to produce materials not present in our original mixture. The strongest infrared unknown absorptions appear in the Cl-O region with no indication of any Cl-F absorption. Further unsuccessful attempts at identification were made by submitting the fractions to gas chromatographic analysis. After several days of storage in a stainless steel cylinder, we could no longer detect the unknown infrared absorption bands indicating the material may not be very stable. We were not successful in subsequent attempts to isolate and identify this small amount of material.

I. Investigations of the Chemistry of Nitrogen Fluorides

Throughout the program reactions were studied periodically in attempts to use the nitrogen fluorides (NF_3, N_2F_4, trans-N_2F_2, cis-N_2F_2) as either fluorinating agents or as agents whereby the difluoroamino group (-NF_2) or the fluorimino group (=NF) could be substituted into oxidizer molecules. Results of these experiments are summarized below.

Nitrogen Trifluoride, NF_3

Several exploratory reactions were carried out using NF_3 in attempts to introduce the difluoroamino group into a ClF_x molecule. A few possible reactions are:

$$NF_3 \quad ClF_3 \longrightarrow F_2NClF_4$$

$$NF_3 + CsClF_4 \longrightarrow CsF + F_2NClF_4$$

$$NF_3 + ClF_5 \longrightarrow F_2NClF_4 + F_2$$
$$\text{etc.}$$

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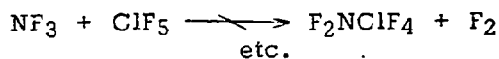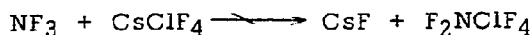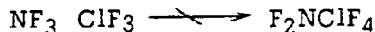
Unfortunately, the high thermal stability of the NF_3 molecule precluded such reactions under the conditions of our experiments

No reaction was detected between NF_3 and ClF_3 at temperatures up to 425 °C and pressures up to 1350 psig. The reactants were recovered unchanged.

NF_3 and ClF_5 did not react after 20 hours at 325 °C (maximum pressure, 2125 psig). There was, however, some thermal decomposition of the ClF_5 to ClF_3 and F_2. The NF_3 was quantitatively recovered.

No reaction occurred between NF_3 and ClO_3F at temperatures up to 475 °C over a period of 18 hours (maximum pressure, 2050 psig). All of the reactants were recovered unchanged.

NF_3 did not react with $CsClF_4$ at temperatures up to 470 °C over a period of 24 hours. The only products observed were the unreacted NF_3 and ClF_3 and CsF resulting from thermal decomposition of the $CsClF_4$.

A mixture of NF_3 and ClF_4SbF_6 was heated at 200° and the products were NF_3, ClF_5, and an off-white solid containing SbF_5 and ClF_5 in a mole ratio greater than one (i.e. SbF_5/ClF_5 1). Since the NF_3 was essentially all recovered, it appears that the pincipal reaction was a simple decomposition of the salt.

$$ClF_4SbF_6 \longrightarrow SbF_5 + ClF$$

Nitrogen trifluoride and difluorochlorine hexafluoroantimonate (V) (ClF_2SbF_6) were combined in a mole ratio 1.3/1 and heated in a monel vessel at several temperatures:

a. At temperatures ranging up to 250 °C and for periods up to 3 hours, there were no signs of reaction and the NF_3 and ClF_2SbF_6 were recovered unchanged.

b. A second experiment at 350° for 23 hours duration indicated no reaction between the NF_3 and ClF_2SbF_6 and the reactants were recovered unchanged.

No reaction occurred between NF_3 and ClO_2 under flow conditions at ambient pressure and temperatures up to 110 °C.

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Tetrafluorohydrazine, N_2F_4

It has been noted that N_2F_4 is a source of NF_2 radicals, and it is conceivable that a radical induced reaction of N_2F_4 with halogen fluorides might lead to unusual difluoroamino-substituted halogen fluorides, e.g.

$$ClF_5 + N_2F_4 \longrightarrow ClF_4NF_2 + NF_3$$

or

$$ClF_3 + N_2F_4 \longrightarrow ClF_3(NF_2)_2$$
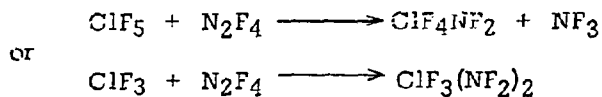
N_2F_4 and ClF_5 did not react at temperatures up to 250°. When reaction finally did occur at 250°C, NF_3 and ClF_3 were the only products suggesting a simple fluorination of N_2F_4 by ClF_5.

$$N_2F_4 + ClF_5 \longrightarrow ClF_3 + 2NF_3$$

In an analogous reaction of ClF_3 with N_2F_4 an exoth. reaction occurred at 250° resulting in fluorination of N_2F_4 by ClF_3. It is interesting to note that the temperature was similar to the initiating temperature of the ClF_5 system above. This suggests that the initiating step is dissociation of the Cl-F bond since N_2F_4 is appreciably dissociated at room temperature.

$$N_2F_4 \longrightarrow 2NF_2$$

$$2NF_2 + ClF_3 \longrightarrow ClF + 2NF_3$$
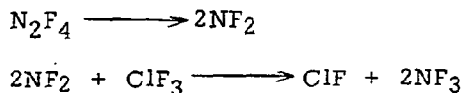
The reaction of ClF with N_2F_4 was carried out to investigate the possibility of ClF fluorinating N_2F_4 and to complete the sequence from ClF_5 and ClF_3. The reaction at 250°C did produce NF_3 and Cl_2 as expected; however, an inordinate amount of NF_3 was found as well as N_2 suggesting a simultaneous thermal decomposition of some of the N_2F_4.

$$N_2F_4 \longrightarrow 2NF_2$$

$$2NF_2 + 2ClF \longrightarrow 2NF_3 + Cl_2$$

$$3N_2F_4 \longrightarrow 4NF_3 + N_2$$

$$4N_2F_4 + 2ClF \longrightarrow 6NF_3 + N_2 + Cl_2$$
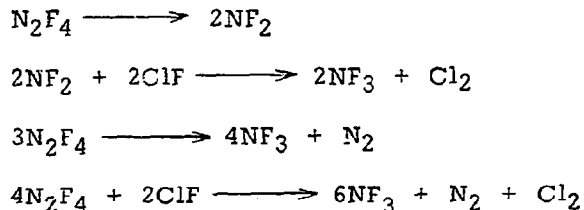
The heterogeneous $CsClF_4$-N_2F_4 system did not interact up to 250°C but at 350°C a rapid reaction occurred giving ClF, NF_3 and N_2 as gaseous products and a solid residue of CsF,

$CsClF_4$ and some Cs_2NiF_6. From the amounts of recovered reactants and products it appears that the primary reactions were simple decompositions

$$3N_2F_4 \longrightarrow 4NF_3 + N_2$$

$$CsClF_4 \longrightarrow CsF + ClF_3$$

$$ClF_3 \longrightarrow ClF + F_2$$
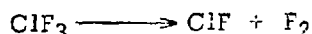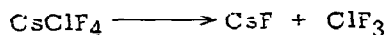
and a fluorination of N_2F_4 by $CsClF_4$ according to the following equation was only secondary:
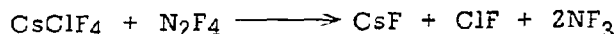
$$CsClF_4 + N_2F_4 \longrightarrow CsF + ClF + 2NF_3$$

The reaction of ClO_2 with F_2 is the preparative method for the synthesis of ClO_2F. Since N_2F_4 can be considered as a pseudohalogen, readily dissociating to $NF_2 \cdot$ radicals, it is reasonable to suppose that N_2F_4 might react with the odd-molecule $ClO_2 \cdot$ to form ClO_2NF_2 as below.
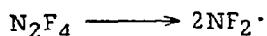
$$N_2F_4 \longrightarrow 2NF_2 \cdot$$

$$NF_2 \cdot + ClO_2 \cdot \longrightarrow O_2ClNF_2$$

The reaction was smooth and the only products isolated were NOF and Cl_2 as well as small amounts of N_2 or F_2. The apparatus apparently contained some HF from the previous use and with the NOF formed minute amounts of solid $NOF \cdot 3HF$. There was no residual ClO_2 in the product mixture and no new or unknown materials were detected.

A reaction between N_2F_4 and ClF_4SbF_6 at 195 °C produced NF_3, N_2, ClF_3, ClF_5, SbF_5 and a mixture $(ClF_x \cdot SbF_6)$ of indeterminate composition. The amount of NF_3 recovered was greater than could be theoretically expected from a thermal decomposition of N_2F_4.

$$3N_2F_4 \longrightarrow 4NF_3 + N_2$$
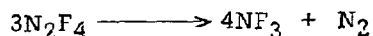
The presence of ClF_5 and SbF_5 is a result of the decomposition of ClF_4SbF_6. The ClF_3 in large quantities indicates that N_2F_4 was fluorinated to NF_3 by the ClF_5. The total reaction is the sum of two reactions:

$$ClF_4SbF_6 \longrightarrow ClF_5 + SbF_5$$

$$ClF_5 + N_2F_4 \longrightarrow 2NF_3 + ClF_3$$
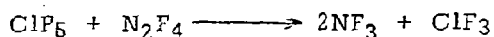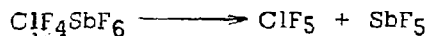
As above, the reaction of N_2F_4 with ClF_2SbF_6 yielded NF_3, N_2, Cl_2, SbF_5 and some (ClF_xSbF_6) of indeterminate composition. From the amount of salt recovered, it was evident that the bulk of NF_3 came from the decomposition of N_2F_4; however, a lesser amount originated with the fluorination of N_2F_4 by ClF_3 and its degradation product ClF producing ultimately Cl_2.

Trans-Difluorodiazine, trans-N_2F_2

An exploratory study was begun to evaluate the feasibility of using N_2F_2 as a fluorinating agent toward ClO_2F and ClO_3F and as a complexing agent toward ClO_2F and ClF_5. The first phases of this work were carried out using an isomeric mixture containing over 95 mole per cent trans-N_2F_2.

No reaction occurred between trans-N_2F_2 and ClO_3F in the temperature range -78° C to 250°C and at autogenous pressures. It is to be noted that the trans-N_2F_2 contained some cis-N_2F_2 and NF$_3$ initially and following exposure at 250°C there was a slight increase in the amount of NF_3 present indicating that some thermal decomposition of the difluorodiazine had occurred.

No reaction was detected between ClF_5 and trans-N_2F_2 in the temperature range -78°C to 250°C. Again thermal decomposition of trans-N_2F_2 was indicated by the slight increase in the relative NF_3 concentration and, with this exception, a nearly quantitative recovery of the starting materials was obtained.

When equimolar amounts of trans-N_2F_2 and ClO_2F were combined at -78°C in a Kel-F trap, the observed pressure was approximately that calculated for an ideal solution; however, a color change occurred immediately on contact of the reactants. The ClO_2F initially was a pale yellow liquid at -78°C and on slow addition of trans-N_2F_2 the color changed to a deep yellow-orange. No phase separation was noted. Infrared analysis of the vapor phase failed to disclose anything other than the reactants and on removing the difluorodiazine the ClO_2F again assumed its pale yellow color. Both reactants were quantitatively recovered.

In a second experiment, a similar but large charge was stored in a monel reactor at 25° thus no color changes could be observed. Infrared analysis of the gas phase indicated only the

starting materials to be present. However, after this charge
was heated at 200°C, a reaction seemed to occur. The pressure
rose steadily to a maximum of 250 psig in the first 4 hours at
200°C and then dropped and leveled off at 100 psig for the
balance of the heating period. Infrared analysis indicated that
ClF_3 was the main product. Present also was some unreacted
ClO_2F, NF_3 (in a larger amount than present in the initial N_2F_2)
and no trace of any difluorodiazine. Mass spectrometric analysis
confirmed the presence of N_2 and O_2. No new or unidentified
materials were detected.

Cis-Difluorodiazine, cis-N_2F_2

Cis-N_2F_2 is known to form complexes with strong Lewis
acids and it was of interest to study the possibility of complex
formation with the Cl-O-F oxidizers. No reaction took place
between cis-N_2F_2 and ClO_2F in the temperature range -78°C
to 180°C. At 180°C, the thermal decomposition of cis-N_2F_2
was noted and the ClO_2F was recovered unchanged at the end
of the experiment.

No reaction was observed between cis-N_2F_2 and ClO_3F
in the temperature range -78°C to 180°C. Conditions were
limited to the point at which the thermal decomposition of cis-
N_2F_2 was detected. A quantitative recovery of ClO_3F was
obtained.

No reaction was observed between cis-N_2F_2 and OF_2 in
the temperature range -78°C to 150°C. At the upper temperature,
the cis-N_2F_2 was almost completely decomposed and a slight
decomposition of OF_2 also occurred but no new products were
formed.

The reaction of cis-N_2F_2 with ClF_5 could form N_2FClF_6
according to the equation

$$N_2F_2 + ClF_5 \longrightarrow N_2F^+ClF_6^-$$
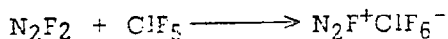
and other possible products can be speculated. The N_2F^+ ion is
known to exist in various compounds but the ClF_6^- ion has yet
to be synthesized. We observed no reaction, however, between

cis-N_2F_2 and ClF_5 in the temperature range $-78\,°C$ to $150\,°C$.
At $150\,°C$, thermal decomposition of the N_2F_2 occurred and also
some degradation of ClF_5 to ClF_3 and F_2 took place.

The expected synthesis of N_2FClF_4 by reaction of cis-N_2F_2
with ClF_3 did not materialize. No reaction was detected between
the gases at temperatures up to $150°$. At the higher temperatures
only the thermal decomposition of cis-N_2F_2 into N_2 and F_2 was
noted in addition to some ClF_5 formed from the subsequent reac-
tion of elemental F_2 with the ClF_3 present.

The reaction of cis-N_2F_2 with ClF did not yield $N_2F^+ClF_2^-$.
As above, no reaction occurred in the $-78°$ to $150°C$ temperature
range. The thermal decomposition of cis-N_2F_2 into N_2 and F_2
was detected above $150\,°C$ in addition to some ClF_3 most likely
formed by a reaction of F_2 with ClF.

J. Electrochemical Studies Relating to the Preparation of New
   Oxidizers

This phase of the program was concerned with a study to
determine the feasibility of preparing new oxidizers by electrolysis
of systems containing as solvents or solutes ClF_3, ClF_5, ClO_2F,
ClO_3F and other halogen fluorides or halogenyl fluorides. As
indicated in several experiments below, the feasibility of this
approach was partially demonstrated by the preparation of ClF_5 by
electrolyses.

Unfortunately many of the halogen fluorides and halogenyl
fluorides of interest as solvents and reactants are poor conductors
and the electrical equivalents which can be passed through a
system are extremely small per unit time. It has been of interest
therefore to screen potential systems for conductivity and to
attempt to provide additives for raising the conductivity to a
practical value.

The cell used performs the dual function of an electrolysis
cell and a conductivity cell and the final design is given in
Fig. 6. This cell was calibrated by measuring the resistance
of standard KCl solutions and the cell constant was determined
as 0.248.

The conductivity values determined during this phase of
the work are summarized in Table II for ready reference and the
discussion of the work is given in the following paragraphs.

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FIGURE 5

ELECTROLYSIS CELL

Top View

Kel-F

B

A ← → A

B

Seal Nut C

Brass

Section A-A

Packing
Box

3/8"

1-3/4"

1-1/4"

1/2"

1-3/4"

1/8"

6"

Electrode
Connector,
Threaded
Nickel

Kel-F

Nickel
Stirrer

3/8"

Loose fit in
socket

Section B-B

1/4" Flare
Fitting

C

Nickel
Electrode

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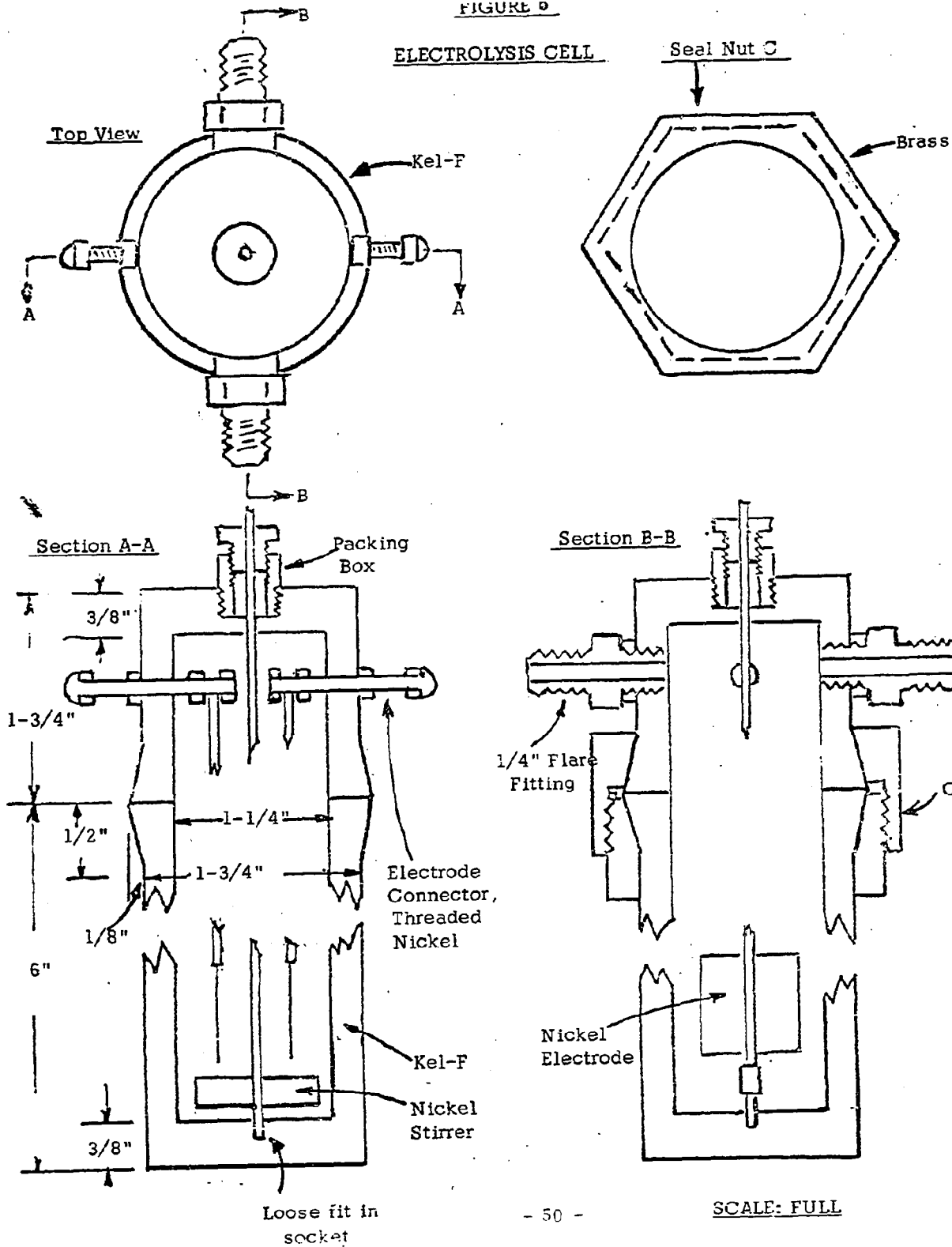
SCALE: FULL

Table II

Conductivities of Oxidizer Mixtures

Solvent	Solute	Mole Fraction Solute	Temp. (°C)	Specific* Conductivity (ohm^{-1} cm^{-1})	Remarks
ClF$_3$			0°	4 x 10^{-7}	Non-conducting (NC)
BrF$_3$			25°	7.53 x 10^{-4}	Purer sample and lower value than that reported by Banks et al. (Ref. 31)
ClF$_5$			-23.9°	<2.11 x 10^{-7}	NC
SbF$_5$			25°	<2.11 x 10^{-7}	NC. Comparable to the value reported by Woolf and Greenwood (Ref. 35)
IF$_5$			25°	5.65 x 10^{-5}	Commercial (99+%); checks with literature (Ref. 36, 37)
ClO$_3$F			-51°	<2.1 x 10^{-9}	NC
BrF$_5$			-51°	1.88 x 10^{-6}	Comparable to reported values (Ref. 38, 39)
			0°	2.18 x 10^{-6}	
			25°	2.?3 x 10^{-6}	
NO$_2$F			-78°	<10^{-6}	NC
HF			-12°	<10^{-6}	NC. See also Ref. 40
ClF$_3$	CsF	0.01	0°	2.3-2.9 x 10^{-4}	Electrolyzed to give ClF$_5$
ClF$_3$	ClF$_2$SbF$_6$	0.013	0°	5.1 x 10^{-4}	Electrolyzed at voltages up to 20 v. D.C. to give quantitative yields of ClF$_5$
ClF$_3$	BrF$_3$	0.098	0°	7.6 x 10^{-6}	NC
	BrF$_3$	0.50	0°	2.4 x 10^{-4}	Unsuccessful electrolysis at 10-11 v. D.C. Conductivity decreased to 1.2 x 10^{-4} ohm^{-1} cm^{-1}. No products isolated.
ClF$_3$	ClO$_2$F	0.044	-12°	<10^{-6}	NC
ClF$_3$	ClO$_2$F	0.043	-12°	12.4 x 10^{-4}	Some ClF$_5$ produced at 12 v. D.C.
	CsF	0.019			
ClF$_3$	IF$_5$	0.153	24°	4.21 x 10^{-6}	NC
ClF$_3$	ClO$_3$F	0.146	-51°	<10^{-6}	NC
SbF$_5$	ClF$_5$	0.103	25°	2.64 x 10^{-5}	Not homogeneous; solids

*Values below 10^{-6} ohm^{-1} cm^{-1} were estimated from resistances measured with a supplementary ohmmeter.

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Table II (Continued)

| Solvent	Solute		Temp. (°C)	Specific Conductivity $(ohm^{-1} cm^{-1})$	
ClF_5	CsF	0.196	-23°	$< 10^{-6}$	NC
ClO_3F	SbF_5	0.040	-51°	$< 10^{-6}$	NC. Solid SbF_5 present
BrF_5	ClF_3	0.130	0°	2.06×10^{-6}	NC
			25°	2.38×10^{-6}	NC
NO_2F	ClF_3	0.5	-78°	$< 10^{-6}$	NC
HF	NO_2F	0.20	-78°	$< 10^{-6}$	NC
HF	ClF_3	0.20	-12°	$< 10^{-6}$	NC
HF	NO_2F	0.166	-12°	$< 10^{-6}$	NC; however, application of 10 v. D.C. resulted in a current flow of 1.3 amps and formation of ClO_2F, ClF_5 and presumably Cl_2.

ClF$_3$/CsF System:

Addition of CsF to ClF$_3$ at a mole ratio of 1 to 100 increased the conductivity from 4×10^{-7} ohm^{-1} cm^{-1} for the pure solvent to a solution of specific conductance of 2.3-2.9×10^{-4} ohm^{-1} cm^{-1}. Electrolysis of this solution at 20 v. D.C. resulted in the formation of ClF$_5$; however, the yields were not determined.

In the work with CsF, the formation of CsClF$_4$ had been postulated as the contributing factor to the appreciable increase in conductivity of the ClF$_3$. However, on using previously prepared CsClF$_4$ it was found that the CsClF$_4$ was not soluble in ClF$_3$ at a mole ratio of 1:100. The specific conductance of the mixture at 0° was about 4.23×10^{-7} ohm^{-1} cm^{-1} and approximately equivalent to that of pure ClF$_3$. The mixture did not conduct appreciable current at applied potentials up to 110 v. D.C.

It is concluded that no CsClF$_4$ was formed in the experiment employing CsF and ClF$_3$. A possible explanation may be an induced ionization of the ClF$_3$ by CsF according to the following equation:

$$ClF_3 + CsF \longrightarrow ClF_2^+ + CsF_2^-$$
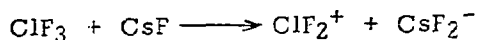
ClF$_3$/SbF$_5$ System:

In view of the poor conductivity of salts supposedly containing the ClF$_4^-$ ion, investigations were carried out on complexes of ClF$_3$ with SbF$_5$ which are postulated to be of the type ClF$_2^+$SbF$_6^-$.

SbF$_5$ was reacted first with ClF$_3$ to yield the white salt and then the required ClF$_3$ was added to produce a mole ratio ClF$_2^+$SbF$_6^-$/ClF$_3$ of 1 to 75.8. The specific conductivity of this solution at 0° was 5.1×10^{-4} ohm^{-1} cm^{-1} and electrolysis was conducted for 5.25 hrs. at increasing voltages of 5, 10, and 20 v. D.C. with respective current flows of 0.005, 0.036, and 0.12 amps. A total of 8.45 milliequivalents of electricity was passed. Fractionation of the evolved gases served to separate ClF$_5$ in virtually quantitative yield from the Cl$_2$ also produced and some small amount of ClF$_3$ which vaporized from the cell.

ClF$_3$/BrF$_3$ System:

The conductivity and electrolytic properties of liquid mixtures of ClF$_3$ and BrF$_3$ were studied using proportions which were respectively high in either one of the components, or in which the proportions of the two were similar.

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The specific conductivity of BrF_3 (m.p. $9°C$) was deter-. mined to be 7.53×10^{-4} ohm^{-1} cm^{-1} at $25°C$ for a material of specified 98.0% minimum purity (Matheson Co.). This was nitrogen-stripped before the conductivity measurement to remove colored material believed to be bromine, as well as any HF.

The observed value is lower than the specific conductivity of 8×10^{-3} ohm^{-1} cm^{-1} for BrF_3 at $25°C$ reported by Banks, Emeleus and Woolf (Ref. 31). They had prepared BrF_3 from the elements, distilled and performed conductivity measurements in a quartz cell with platinum electrodes. Our cell was constructed of Kel-F, with nickel electrodes. In a continuation of their studies, Emeleus and Woolf (Ref. 32) demonstrated a quantitative reaction between SiO_2 and BrF_3 in accord with the reaction $3SiO_2 + 4BrF_3 \longrightarrow 3SiF_4 + 3O_2 + 2Br_2$ from which all products should be ultimately volatile. Rather surprisingly, their experiment was conducted in silica equipment. It appears, in any event, that the difference between our observed conductivity value for BrF_3 and the previous report may be attributable to purity differences.

The conductivity of a solution of 1 mole of BrF_3 in 9.2 mole ClF_3 was 7.6×10^{-6} ohm^{-1} cm^{-1} ($0°$) and too low to attempt electrolysis. The concentration of BrF_3 was increased until it was equimolar with ClF_3. The specific conductivity of this solution was 2.4×10^{-4} ohm^{-1} cm^{-1} ($0°$) and the solution was electrolyzed at 10-11 v. D.C. with a total of 286 coulombs passed. We were not able to isolate products in order to explain the current flow in the cell although some inconclusive evidence was obtained suggesting that ClF may have been a product.

A mixture of 1 mole ClF_3 to 9.29 moles BrF_3 was electrolyzed at an average potential of 20 volts (average 0.13 amps) for 17 hours. No volatile products were noted in the traps downstream of the cell.

The residual BrF_3 solution was colored dark orange-brown. This is attributed to the presence of bromine which could be swept from the cell by nitrogen and condensed. Claasen, Weinstock and Malm (Ref. 33) noted that pure BrF_3 reacts slowly with nickel to form reddish products which may be Br_2 or BrF. Our nickel electrodes were tarnished although not corroded sufficiently to account for the quantity of Br_2 and it is believed the Br_2 is a direct or indirect result of electrolysis.

During electrolysis of the ClF_3/BrF_3 solution, the conductivity decreased from 1.9×10^{-4} to 1.2×10^{-4} ohm^{-1} cm^{-1}. Banks et al. (loc. cit.) observed the same phenomenon on electrolysis of pure BrF_3 and postulated the following mechanism:

$$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$$

$$2BrF_2^+ + 2e \longrightarrow BrF_3 + BrF \text{ (brown, unstable)}$$

$$2BrF_4^- \longrightarrow 2e + BrF_3 + BrF_5 \text{ (colorless)}$$
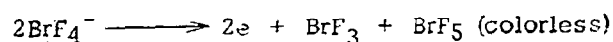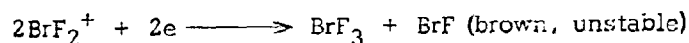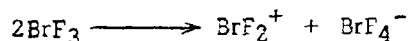
The formation of BrF and BrF_5 in the BrF_3 would decrease the conductance simply by dilution. The above mechanism is consistent with our observations since BrF is an unstable material forming the Br_2 observed in our cell.

$$3 BrF \longrightarrow Br_2 + BrF_3 \qquad \text{(Ref. 34)}$$
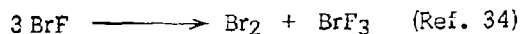
It should be noted that Banks et al. proposed the above mechanism partly to explain the absence of polarization in their work. In our studies polarization was observed and could be eliminated temporarily by reversing the polarity. This may be due to some unknown influence of the dissolved ClF_3.

ClF_5/SbF_5 System:

The specific conductivity of ClF_5 prepared in this laboratory was determined to be $< 2.11 \times 10^{-7}$ ohm^{-1} cm^{-1} (the lower limit of our conductivity bridge) at -78°C and at -23.9°C, and is probably somewhat lower, i.e., $< 10^{-7}$ ohm^{-1} cm^{-1}. The fact that there was no observable increase in conductivity between dry-ice temperature and -23.9°C, nearly the boiling point of ClF_5, seems to indicate that the conductivity of this substance is very low and the pure compound would be impractical as an electrolyte. This was, of course, the sole purpose of our conductivity determination.

In a separate experiment doubly-distilled SbF_5 was charged to the conductivity cell under dry-box conditions and the specific conductivity was found to be $< 2.11 \times 10^{-7}$ ohm^{-1} cm^{-1} at 25°C. The specific conductivity of SbF_5 has been reported as $< 10^{-9}$ ohm^{-1} cm^{-1} (Ref. 35). The value determined in this laboratory appears in keeping with the prior reports.

The properties of the system mixed SbF_5-ClF_5 were than explored using a high ratio of SbF_5. Final proportions were in the mole ratio 8.72 SbF_5/ClF_5. Since SbF_5 freezes at 7°C, the reaction was initiated at 10°C and the ClF_5 was added in increments as a gas under its own vapor pressure. A slightly yellow solid was formed immediately on addition of ClF_5 to SbF_5 and persisted even though the cell was allowed to warm to 25°C. Mixing was extremely slow because of the density and viscosity of the SbF_5, coupled with the formation of a crust of complex $ClF_5 \cdot SbF_5$ on the surface of the liquid. Slight warming did tend to melt the complex, but this could not be carried to the point of homogeniety.

A final measurement showed the specific conductivity of the inhomogeneous liquid-solid system to be 2.64×10^{-5} ohm^{-1} cm^{-1} at 25-30°C. The enhanced conductivity of the system indicates that the $ClF_5 \cdot SbF_5$ complex is probably an ionic species such as $ClF_4^+SbF_6^-$.

During overnight storage of the cell containing SbF_5 and the complex, a severe crack developed on the interior wall of the cell (see Fig. 5). On warming slightly to dissolve the complex, further extensive cracking occurred, with leakage from the cell. The experiment, including contemplated electrolysis, was abandoned of necessity.

Subsequent studies of the ClF_5-SbF_5 system was carried out at low temperatures to minimize stress cracking of the cell. At -23°, it was observed that a combination of ClF_5 and SbF_5 in a mole ratio of 21.5:1 consisted of supernatant liquid ClF_5 above a solid mass of frozen SbF_5 containing solid ClF_4SbF_6. The specific conductance of the non-homogeneous system was equivalent to that observed for pure ClF_5.

The presence of the ClF_4SbF_6 was indicated by a mass balance of the ClF_5 used, and recovered, as well as evidence of stress cracking in the Kel-F cell due to overnight storage of non-volatile residual solids.

The non-conductivity of the liquid ClF_5 suggests that none of the complex had dissolved. Whether this was the result of inherent insolubility or poor mixing is not known. The ionic nature of the ClF_4SbF_6 complex was suggested by an experiment using a mole ratio of 1 ClF_5 to 8.72 SbF_5 in which the complex was formed and increased the conductivity of the SbF_5 from $<2.11 \times 10^{-7}$ ohm^{-1} cm^{-1} to 2.04×10^{-5} ohm^{-1} cm^{-1}.

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ClF_5/Metal Fluoride System:

Since CsF was observed to increase the conductivity of ClF_3, it was of interest to investigate the conductivity of alkali metal fluorides and, for comparative reasons, that of CsF in ClF_5.

The specific conductance of a mixture containing a mole ratio of 54.1 ClF_5/CsF at $-23°C$ was determined to be $< 2 \times 10^{-9}$ ohm^{-1} cm^{-1} by supplementary observation of resistance with a volt-ohmeter. However, the validity of the determination was questioned because a liquid product, believed to be a hydrated acid fluoride, was recovered as a final cell residue. Repetition of the experiment using ClF_5 freed of HF at a mole ratio of 50 ClF_5/CsF confirmed the specific conductance of the system to be $< 10^{-6}$ ohm^{-1} cm^{-1}. A solid product which was evidently CsF containing absorbed ClF_5 was finally obtained, but mass balance did not indicate the formation of a complex. In both experiments, CsF was insoluble in ClF_5 so that the low conductance value and failure to pass current were doubtless characteristic of ClF_5.

Anhydrous KF was insoluble in liquid ClF_5 at $-23°$ at a mole ratio of 26.3 ClF_5/KF. The specific conductance of the mixture was $< 10^{-6}$ ohm^{-1} cm^{-1}, which was no doubt that of ClF_5. There was no evidence of complex formation between ClF_5 and KF.

ClF_3/ClO_2F System:

In previous studies (Ref. 23) it had been found that ClO_2F will dissolve readily in ClF_3 to give a dense solution attractive as a mixed oxidizer. In addition the sensitivity of ClO_2F to hydrolysis by moist air seemed to be moderated by solution. Although this could be attributed to dilution, it seemed worthwhile to study the liquid system for evidence of dissolved ionic compounds. The conductivity of a solution of ClO_2F in ClF_3 was determined at $-12°C$, first at a mole ratio of 31.8 ClF_3/ClO_2F, then at 21.7 ClF_3/ClO_2F. The specific conductance of each system was $< 10^{-6}$ ohm^{-1} cm^{-1}. This value if of an order similar to the conductivity of ClF_3. It is concluded that ClO_2F must also have a low conductivity since addition of ClO_2F to ClF_3 did not alter conductance, even on increasing the proportion of ClO_2F.

Since fluorination of ClO_2F is an attractive route to new oxidizers and since ClO_2F is sensitive to protonic solvents, it was evident that this compound must be studied in compatible solvents such as ClF_3 containing additives such as CsF to increase the conductivity.

The ClF_3-CsF system was the conducting medium and the source of fluorine on electrolysis which could be replenished by subsequent additions of ClF_3. The ClO_2F is typical of intermediates which can be dissolved in the ClF_3-CsF mixture and, although non-conducting themselves, will be fluorinated on electrolysis. There is thus an analogy to the Simons cell and the electrolysis of hydrocarbons in KF-HF systems.

The addition of CsF to the liquid system ClF_3/ClO_2F at $-12°C$ produced an increase in conductivity, the specific conductance being 12.4×10^{-4} ohm^{-1} cm^{-1} at a mole ratio of 50 $ClF_3/2.3$ ClO_2F/CsF. However, the CsF was incompletely soluble and in addition, flocculent material of an apparently different character formed on first storage at $-78°$; persisting on warming to $-12°$. Appearance of the flocculent material was accompanied by a small decrease in specific conductance to 8.43×10^{-4} ohm^{-1} cm^{-1}. Subsequent analysis of this system indicated that the presence of ClO_2F prevented dissolution of the CsF in the ClF_3 solvent and that the observed flocculent precipitate was pure CsF.

ClF_3/IF_5 System:

The specific conductance of commercial IF_5 (99+%) was determined to be 5.65×10^{-5} ohm^{-1} cm^{-1} at $25°C$, and 4.02×10^{-5} ohm^{-1} cm^{-1} in a mixed solid-liquid phase system at the freezing point of $9°C$. These data compare favorably with the values reported by Woolf (Ref. 36) and by Rogers et al. (Ref. 37).

IF_5 was completely soluble at $0°C$ in ClF_3 and a mixture containing a mole ratio of 6.76 ClF_3/IF_5, had a specific conductance at this temperature of 2.43×10^{-6} ohm^{-1} cm^{-1}. At $24°C$ and a mole ratio of approximately 5.54 ClF_3/IF_5, the specific conductance increased only slightly to 4.21×10^{-6} ohm^{-1} cm^{-1}. Since it appeared that the conductivity values observed resulted from the dilution of IF_5 without the formation of conductive species in ClF_3, such mixtures were not explored further. There

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was no indication of an induced ionization as given in the equation below and the conductivity was too low for practical electrolysis.

$$IF_5 + ClF_3 \rightleftharpoons ClF_2^+ + IF_6^-$$
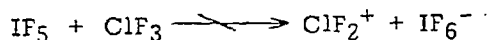
ClF_3/ClO_3F System:

The specific conductance of ClO_3F (b.p. -47°C) was determined to be $< 2 \times 10^{-9}$ ohm^{-1} cm^{-1} at -51°C, in good agreement with a previously reported value (Ref. 38). The specific conductance of a ClF_3/ClO_3F mixture in the respective mole ratio 5.83/1 was observed to be $<10^{-6}$ ohm^{-1} cm^{-1} at -51°C. Because both components of the mixture are poorly conductive, the low conductivity value of the mixture indicated the absence of any ionic species. ClO_3F alone or with ClF_3 did not pass current under applied potential, and electrolysis was not feasible.

$$ClO_3F \rightleftharpoons ClO_3^+ + F^-$$

$$ClO_3F + ClF_3 \rightleftharpoons ClO_3^+ + ClF_4^-$$
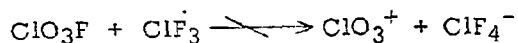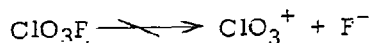
A ternary mixture composed of a mole ratio of 29.3 ClF_3/4.86 ClO_3F/CsF contained undissolved solids at -51° and was observed to have a specific conductivity of 1.24×10^{-7} ohm^{-1} cm^{-1}. Electrolysis was impractical since the system did not conduct appreciable current.

The conductance of the ternary system was less than that of the initial ClF_3/CsF mixture before adding ClO_3F, indicating that the latter served mainly as a diluent and did not form ionic species with CsF. As noted above, a mixture of ClF_3 and ClO_3F was non-conductive, so that the meager conductivity detected for the ClF_3/ClO_3F/CsF system appeared to be due to a ClF_3-CsF complex, possibly $ClF_2^+CsF_2^-$ as proposed above.

ClO_3F/SbF_5 System:

The possible formation of complex ions by ClO_3F was explored further by observation of a mixture containing a mole ratio of 24.3 ClO_3F/SbF_5. The specific conductance of the system was $< 10^{-6}$ ohm^{-1} cm^{-1} at -51°C. The SbF_5 (m.p. 7°C) appeared to disperse throughout the ClO_3F as fine, white suspended particles on stirring. The mixture was non-conductive under an applied potential of 107 volts D.C., so that electrolysis was not possible. Qualitative

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tests on the non-volatile material recovered showed it to be pure antimony fluoride. The conclusion that ClO_3F did not form an ionic complex with SbF_5 agrees with other studies made in this laboratory employing pressure techniques.

ClF_3/BrF_5 System:

The specific conductance of commercial BrF_5 (HF-free) was determined to be 1.88×10^{-6} ohm^{-1} cm^{-1} at $-51°C$ (m.p. $-62°$), 2.18×10^{-6} ohm^{-1} cm^{-1} at $0°$ and 2.73×10^{-6} ohm^{-1} cm^{-1} at $25°$ (b.p. $40°$). The results at $-51°$ and $0°$ are comparable to values reported for a similar commercial material (Ref. 38); but, as expected, the value at $25°$ is somewhat above the conductance of 9.1×10^{-8} ohm^{-1} cm^{-1} reported for a "carefully purified" sample (Ref. 39). As noted below, some Br_2 may have been present in the BrF_5.

A homogeneous solution containing a mole ratio of 6.39 BrF_5/ClF_3 exhibited a specific conductance of 2.06×10^{-6} ohm^{-1} cm^{-1} at $0°$ and 2.38×10^{-6} at $25°$. Neither the pure BrF_5 nor a solution with ClF_3 passed more than one milliampere current under an applied potential of up to 108 volts D.C. The addition of a slight amount of ClF_3 to the BrF_5 caused the color of the BrF_5 to change from a dark red brown to a clear faint amber. However, because no conductivity changes were noted and no solid residues were recovered, it is thought that the color change indicated the fluorination of a small amount of elemental bromine contaminant by the ClF_3.

The Ternary $NO_2F/ClF_3/HF$ System

The conductivities of liquid mixtures containing NO_2F, ClF_3 or HF were observed while employing the constituents in various combinations, proportions and orders of addition. The specific conductances of the individual constituents were found to be $< 10^{-6}$ ohm^{-1} cm^{-1} at the temperatures noted below. The binary mixtures (NO_2F/ClF_3, HF/NO_2F, HF/ClF_3) and ternary mixtures were similarly non-conductive. Conductivity measurements involving NO_2F (b.p. $-72°C$) alone or with either HF or ClF_3 were made at $-78°$ because of pressure limitations, but observations of the con-ductivities of HF and ClF_3 were made at $-12°$ or above. The latter temperature was used in studying ternary mixtures containing excess HF, since these exhibited relatively low vapor pressure at $-12°$. However, when equimolar quantities of the three components were used, the high gas pressure which developed prevented warming much above $-78°$.

An equimolar mixture of NO_2F and ClF_3 at $-78°$ contained a small quantity of yellowish white dispersed solids identified as NO_2ClF_4. This material is insoluble in either reagent and did not increase the conductivity of the system. Addition of HF to produce an equimolar ratio of $NO_2F/ClF_3/HF$ produced additional solids, presumably $NO_2F \cdot XHF$, but the HF was insufficient to complex all the NO_2F since pressure developed on warming above $-78°$. The same adduct was also formed on addition of one mole of NO_2F to 4 moles of HF at $-78°C$. In contrast, a solution of one mole ClF_3 in 4 moles of HF was a homogeneous clear liquid. Ternary mixtures containing excess HF (mole ratio about $4HF/ClF_3/NO_2F$) developed relatively little pressure at $-12°$, and probably contained sufficient HF to completely complex the NO_2F.

In view of the low conductance values observed, it was surprising to find that a momentarily applied potential of 10 volts D.C. resulted in a current flow as high as 1-2 amperes in ternary mixtures with excess HF at $-12°$. This property was shown to a limited degree by HF alone, but not by NO_2F, ClF_3, or their mixture. Action on the nickel electrodes at the higher amperages was indicated by darkening, sometimes with formation of solids.

In preparing ternary mixtures containing excess HF (mole ratio about $4HF/NO_2F/ClF_3$), the order of addition appeared to have some influence on the products recovered. Addition of ClF_3 to NO_2F in HF at $-196°$ resulted in a mixture of liquids and solids which persisted on warming to $-78°$. This order would have permitted preliminary formation of $NO_2F \cdot HF$ adducts. The ternary system passed about .05 amp. at $-78°$ and over 1 amp. at $-12°$. However, when NO_2F was added to ClF_3 in HF at $-196°$, a pressure increase was briefly noted on warming to $-78°$ and a liquid product resulted. If $NO_2F \cdot XHF$ or NO_2ClF_4 were present, they or other products were soluble. This ternary system passed about 0.6 amp. at $-78°$ and 2 amps. at $-12°$.

Products from the electrolysis of the ternary $NO_2F/ClF_3/HF$ mixtures at $-12°$ were analyzed and were found to be ClO_2F, ClF_3 and ClF_5 but the pressure of the samples further indicated the presence of a considerable portion of a gas nonabsorbing in the infrared, presumably Cl_2. The liquid remaining in the conductivity cell after warming to $45°$ was also examined by infrared and several runs produced samples with consistent absorption at 4.2μ, commonly associated with nitrogen triple bonding. This material was never identified.

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III. Appendix

1. Description and Layout of Adiabatic Calorimeter

The adiabatic calorimeter and temperature measuring equipment were contained within a large Plexiglass enclosure ($T=25° \pm .05°C$) and located in a small laboratory where the room temperature was maintained at $23.5 \pm 1°C$. This provided a constant heat leak from the Plexiglass enclosure and easy temperature control within the enclosure. Access to instruments within the enclosure was through gum rubber "iris diaphragm" ports (cf. Fig. 7). Dials were adjusted and electrical balances were made using "poke rods" thereby eliminating thermal gradients from the human hand. This is illustrated in Fig. 7.

A platinum resistance thermometer was used to determine temperature rises in the calorimeter. The thermometer was connected to the measuring bridge (G-1 Mueller Bridge, Leeds and Northrup) through a mercury commutator (No. 8068, Leeds and Northrup) designed to permit cancellation of lead resistance differences.

A 1000-ohm resistor in series with a slow bleed 2-volt cell (Willard DD-S-1) intentionally limited the current in the thermometer circuit to 1.5 milliamps. This current was below the 2 milliamp continuous flow used in calibration of the thermometer at the National Bureau of Standards. This limitation decreased the sensitivity of the null point galvanometer (No. 2430a, Leeds and Northrup) but essentially eliminated error due to heating of the resistance element in the thermometer.

It had been experimentally determined, by measurement of the triple point of water, that temperatures could be measured to an accuracy of $0.001°C$ with an error of $\pm 0.0005°C$.

The linear power equation established by the National Bureau of Standards during calibration of the platinum resistance thermometer was programmed for the Bendix Model G15 computer and a print out of measured resistances versus temperature was obtained from $23°C$ to $30°C$ in intervals of $0.001°C$. This permitted immediate and convenient determination of temperature in degrees Centigrade.

It is important to note that during preliminary runs with the NH_4ClO_4- CO system it was found that the use of a platinum sample cup and support and a gold-plated calorimeter were found necessary to eliminate the formation of iron carbonyl by the reaction of the bomb alloy with the excess CO at the high combustion temperature.

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Fig. 7
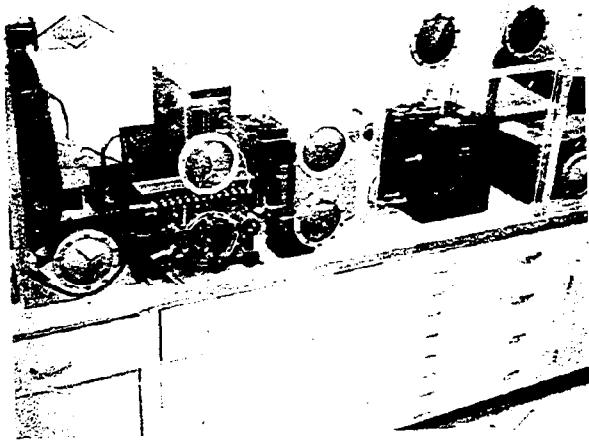
LAYOUT OF CALORIMETER
AND
SUPPORTING EQUIPMENT

For calibration a total of ten combustions were carried out using N.B.S. standard benzoic acid under certificate conditions. The final accepted heat capacity was 2455 ± 2.8 cal/°C. Additional blank runs were carried out to determine the heating of the calorimeter due to electrical input to the ignition wire as 1.1 cal. The correction in the heat capacity of the calorimeter due to a substitution of CO for O_2 amounts to C.025 cal/°C and was considered negligible.

The NH_4ClO_4 pellet was supported in a platinum cup within the gold-plated calorimeter and ignition was by an electrically heated platinum fuze. Prior to ignition, the loaded bomb was flushed at least three times with CO at 30 atmospheres pressure to eliminate atmospheric oxygen. The results of the experiments are summarized in Table I.

At the conclusion of the run the gases within the bomb were examined by infrared analysis for traces of nitrogen oxides indicating incomplete combustion. Vapor chromatographic analysis previously showed that the vapor phase was composed only of N_2, CO, CO_2 and water vapor.

The gaseous products were then dried by passing over $MgClO_4$ and adsorbed on ascarite for a direct determination of the carbon dioxide evolved. The liquid phase remaining in the bomb was quantitatively removed and analyzed for acid titer, chloride ion, and anionic and cationic nitrogen. These data were used as confirmatory evidence for completeness of combustion.

2. Synthesis of ClO_2

A 1:4 molar mixture of $NaClO_3$ (21.2 g.) and $H_2C_2O_4 \cdot 2H_2O$ (100.0 g.) was added dry to a 500-ml. 3-necked round bottom flask. Distilled water (25 ml.) was added to the mixture and the flask was immersed in a water bath. A flow of nitrogen (75-100 cc./min.) was started and the reaction flask was slowly heated. ClO_2 generation began at 40-45° and the nitrogen flow was increased to about 300-350 cc./min. The bulk of the ClO_2 was evolved between 45°-55°C. The temperature was slowly raised following diminution of gas evolution and was maintained in the range 65°-70°C. When generation ceased the reaction mixture was quenched with 100-150 ml. distilled water. The ClO_2, trapped out at -78°C, was purged well with nitrogen and then immersed in a -5° to -8°C salt bath to permit the ClO_2 to liquefy and to dispel any dissolved CO_2. After about 5 minutes under these conditions, the -78°C bath was again placed around the ClO_2 and maintained during temporary storage of the ClO_2.

$$2NaClO_3 + 2H_2C_2O_4 \cdot 2H_2O \longrightarrow 2ClO_2 + 2CO_2 + 2H_2O + Na_2C_2O_4$$
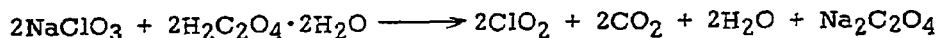
3. (U) Synthesis of ClO_2F

The liquid ClO_2 was immersed in a $0°C$ salt bath and vaporized with a nitrogen flow set at about 250 cc./min. This permitted a sufficient dilution to avoid explosions and also provided a reasonable rate of consumption of the ClO_2. The nitrogen-diluted ClO_2 was led into a copper coil reactor through which F_2 gas was passed at a flow rate of up to 250 cc./min. The reactor was made of 3/8" copper tubing and various lengths gave reactor volumes of 11-1230 ml. (residence times of 4 seconds to 4 minutes). The most satisfactory results were obtained with a 1230-ml. reactor volume and 4-min. residence time. The product gases were passed through a 1/4" copper coil of 85-ml. volume heated to 105-110°C (15-second residence time). This coil was used to effect thermal decomposition of residual ClO_2 to Cl_2 and O_2. The final product had been trapped out as a solid at -183°C together with solid Cl_2 and liquid F_2, N_2, and O_2. The Cl_2, F_2, N_2, and O_2 were easily removed by fractional condensation techniques. (Note: Since F_2 was removed at low temperatures, no reaction with solid Cl_2 was observed. The formation of ClF_3 was also not observed in the heated coil.) The water white produce following purification was stored in a stainless steel cylinder at -80°C.

4. (C) Preparation of ClF_5

CsF (13.4 g., 0.088 moles) was charged to a nickel autoclave. After evacuation, the autoclave was cooled to -78°C and 21.6 grams of ClF_3 (0.23 moles) was vacuum transferred to the autoclave. The approximate mole ratio of ClF_3 to CsF was 2.5:1.0. The autoclave was placed into a jacket heater and maintained at 80°C ± 2° for 24 hours, developing a maximum pressure of 80-85 psig at this temperature.

After 24 hours, the autoclave was cooled in a water bath to 20-25°C and all the volatiles were pumped off. Calculations based on ClF_3 recovered indicate the ClF_3 retained by the CsF on a 1:1 mole basis was approximately 85-90% of theoretical.

The evacuated autoclave was cooled to -196°C and 0.5 moles of fluorine was introduced to a total pressure (at 25°C) of 610 psig. The $F_2/CsClF_4$ mole ratio was approximately 6/1.

The autoclave was again placed in the jacket heater and maintained at 150° ± 2°C for 24 hours and then cooled to -125° to -130°C. At this temperature all the excess F_2 was vented off until the autoclave was at atmospheric pressure. The autoclave was then closed, warmed to ambient temperature and all the volatile products condensed at -196°C. The residual F_2 was removed under vacuum.

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The product was then fractionated through a -100°, -140°, -196°C train and ClF$_5$ was concentrated in the -140° trap.

Infrared analysis of the product indicated primarily ClF$_5$ with some slight contamination by ClO$_2$F, SO$_2$F$_2$ and SF$_6$. (The source of the sulfur compounds is the original fluorine used in the preparation.) A comparison of our observed absorption bands with those published by Rocketdyne (Ref. 3a) are given below. Our spectrum was obtained on a P-E Model 337 Grating Spectrophotometer (2-25 μ range).

Rocketdyne	Our Observed Bands
780 cm.$^{-1}$	780 cm.$^{-1}$ with a shoulder at 790 cm.$^{-1}$
720 cm.$^{-1}$	720 cm.$^{-1}$
630 cm.$^{-1}$	630 cm.$^{-1}$ \
	620 cm.$^{-1}$ } Triplet
	610 cm.$^{-1}$ /
540 cm.	545 cm.$^{-1}$ \ Doublet
	535 cm.$^{-1}$ /
495	490 cm.$^{-1}$ (est. 492-493)
480	480 cm.$^{-1}$
300	(Beyond the range of our instrument)

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Pennsalt Chemicals Corp.	Confidential
	2b. GROUP

3. REPORT TITLE

Synthesis of Inorganic Oxidizers. (U)

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Summary Report for Period Aug. 1, 1962 to April 1, 1966

5. AUTHOR(S) *(Last name, first name, initial)*

Gardner (David M.) and Bartoszek (Edward J.) et al.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May, 1966	69	33

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF 04(611)-8518	
b. PROJECT NO. 3148, Task No 314804,	113989 Final
c. ARPA Order No 352	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d. (Amend # 4)	

10. AVAILABILITY/LIMITATION NOTICES

Qualified requesters may obtain copies of this report from DDC

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U. S. Air Force Systems Command Research and Technology Div. Rocket Propulsion Lab. Edwards, California

13. ABSTRACT

Research was carried out on the synthesis of new oxidizers composed of combined forms of chlorine, oxygen, and fluorine. Experimental techniques used included high pressure - high temperature reactions, arc and glow discharge reactions, and electrochemical reactions in interhalogens and other active fluorinating solvents (U).

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Solid Propellants						
Synthesis						
Inorganic oxidizers						
Halogen fluorides						
Chlorine oxides						
Nitrogen fluorides						

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